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CONTENTS

THIS MONTH'S COVER

• *Group of 1600-barrel Hortonspheres installed at United Gas Pipe Line Company's Carthage, Texas, cycling plant. Service life of tanks such as pictured is extended through application of proper coatings to protect against atmospheric attack. Tank corrosion in general has proved a costly item to management in all industries where tanks are used. And to help management reduce this toll, NACE has established a Technical Committee to study the problem. Photograph courtesy Chicago Bridge & Iron Company.*

"You can't dock there, you're much too close to my

THE CAPTAIN is really not so unreasonable as he seems.

On land he's probably very friendly indeed. But, right now he is suffering from a bad case of *galvanic corrosion phobia.* It *could* happen to you . . . and maybe *has.* For on land or sea a good deal of obscurity exists about galvanic corrosion. Like anything not fully understood, it may lead to strange conduct.

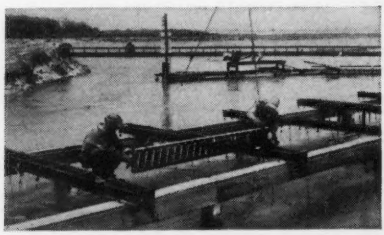
The Captain's fears arise from the fact that the smaller vessel is sheathed with a metal lower in the galvanic series than his own steel hull-plates. For generations, some sailors have been wont to blame a leaky hull on galvanic effects from an adjacent ship. According to the distinguished authority on metal corrosion at Cambridge University, Prof. U. R. Evans, *"Copper ships have long enjoyed an evil reputation as neighbors for steel ships in port."**

Waiving the moral question, whether any ship has a right to "enjoy" an evil reputation, in certain exceptional cases this reputation may have been deserved. For instance, some authorities consider galvanic effects between a rapidly-moving propeller and steel hull-plates a serious cause of ship corrosion, especially at points where there is a break in the scale or paint. With the two different ships shown above, the galvanic effect would be serious only at breaks in the coating on the steel ship, and then only if there were actual metallic contact between the two ships for a prolonged period.

*"Metal Corrosion, Passivity and Protection," by U. R. Evans, Longmans Green & Co., New York, page 523, (1946).

NOT ALWAYS GUILTY

Galvanic or bi-metallic corrosion, as it is sometimes called, has acquired an unduly bad name in many quarters. Obscure difficulties are often unreasonably attributed to it. In some quarters, galvanic effects



Underwater corrosion testing by Inco corrosion engineers at Kure Beach, North Carolina. A rack of metal specimens is shown being lowered into the ocean.

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Resistance of Aluminum to Corrosion in Solutions Containing Various Anions and Cations*

By A. B. McKee and R. H. Brown***

THE RATE of corrosion of aluminum is controlled by the protective oxide film which forms when an aluminum surface is exposed to the atmosphere. This film, although very thin and usually invisible to the unaided eye, is highly protective and resists attack under many conditions of service. It is to this inert film that aluminum owes its inherent high resistance to corrosion. The corrosion mechanism for aluminum in neutral or nearly neutral solutions is usually accompanied by the formation of additional hydrated aluminum oxide which deposits on the surface of the metal and tends to serve as a barrier to further attack. For this reason the attack by some solutions may be relatively rapid at first, but as the insoluble products of the reaction are formed, an adherent, continuous film covers the metal which further reduces the probability of contact of the solution with the underlying metal and as a result the corrosion stops or is reduced to a very low rate. In solutions which tend to dissolve the existing oxide coating or in solutions which tend to produce highly soluble corrosion products, the attack would be expected to be relatively greater than in solutions in which the film is spontaneously healed. Therefore, in many solutions the corrosion rate will be controlled by the solubility of the corrosion products, which in turn is not necessarily related to the acidity or alkalinity of the solution.

Borgmann[1] has shown that the effect of cations on the rate of corrosion of mild steel is appreciable. In his tests, the effect of chlorides of a wide variety of metals was studied. The corrosive effect of various cations on mild steel was found to increase in this order: Mg^{++} (magnesium), Cd^{++} (cadmium), Mn^{++} (manganous), Ca^{++} (calcium), Sr^{++} (strontium), Ba^{++} (barium), Li^{+} (lithium), Na^{+} (sodium), K^{+} (potasium), Al^{+++} (aluminium), NH_4^{++} (ammonium), Cr^{+++} (chromium), Fe^{+++} (ferric). He concluded that if the anion in neutral solution is non-oxidizing or non-reducing and forms soluble primary products with the metal, the rate of corrosion depends on the nature of the cation.

Since the ability of aluminum to

★ A paper presented at the Annual Meeting of NACE in Chicago, Ill., April 7-10, 1947.

* Chemical Metallurgy Division, Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pennsylvania.

** Chief, Chemical Metallurgy Division, Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pennsylvania.

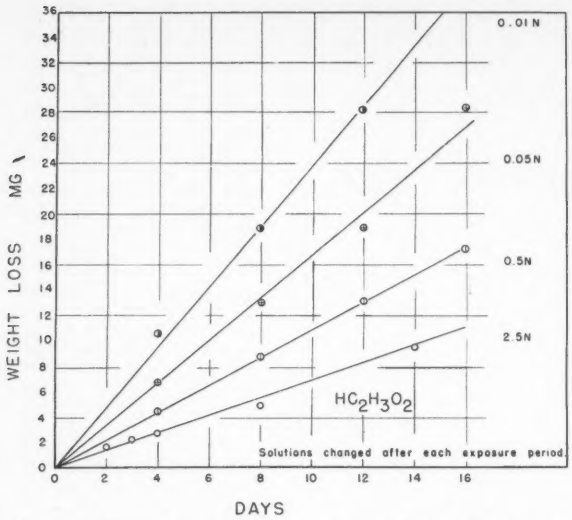

Figure 1—Effect of exposure time on weight loss of aluminum (2S-1/2H). Specimens exposed in acetic acid solutions.

resist corrosion depends to a large extent on the presence of an adherent, continuous oxide film, the corrosiveness of solutions is influenced to a great extent by the ability of the ions to penetrate this coating. Britton and Evans[2] report that in general the penetrating power of anions may be related to their size, solubility, and diffusivity. They found by means of experiments, in which they measured the leakage current passing to an aluminum anode covered with an oxide film of low electric conductivity, that the penetrating power of anions in decreasing sequence is chloride, bromide, iodide, fluoride, sulfate, nitrate, and phosphate. Small anions, such as chloride, bromide, and iodide show high rates of penetration; the fluoride anion, which probably forms a complex ion, has a lower rate of penetration. Sulfate and nitrate anions have still lower rates of penetration. The lower value for nitrate anion may be due to its oxidizing character. Phosphate anions have a yet smaller penetrating rate as a result of the sparing solubility of aluminum phosphate.

Akimow and Glukova[3] have reported some data on the effect on aluminum of the anions chloride, sulfate, and nitrate in solutions acidified with hydrochloric, sulfuric, or nitric acids or made alkaline with sodium hydroxide to obtain the desired pH and, at the same time, holding the solution one normal with respect to the given anion by the addition of the proper sodium salt. Chlorides were shown to increase the corrosion in acid solutions to a far greater extent than either nitrates or sulfates. However, in solutions made highly alkaline with sodium hydroxide, the effect of the three different anions was of the same order.

Purpose of Investigation

This investigation had a twofold purpose: (1) to study the effect of various anions and cations on the corrosion rate of aluminum, and (2) to establish concentrations of acids and bases for a number of different solutions within which aluminum could be safely employed.

This investigation involved preliminary work to determine the size

of specimen, volume of solution, and the frequency of solution changes which could be best adopted for beaker-type tests, and still hold the variation in concentration during exposure to a minimum. It was found that if 0.064-inch by 0.5-inch by 4-inch specimens of 2S-1/2H* aluminum were exposed in 500cc of solution and the solutions were changed after 24 hours, a variation of not more than 0.5 units from the original pH could usually be maintained.

Preliminary tests were also necessary to establish the shape of the "time versus weight loss" curves for the various type of solutions. In solutions such as acetic acid and sodium hydroxide (see Figures 1 and 2) the weight loss of aluminum varies linearly with time. For this reason the corrosion rate is based on two-day exposure periods for all solutions whose "time versus weight loss" curves are straight lines.

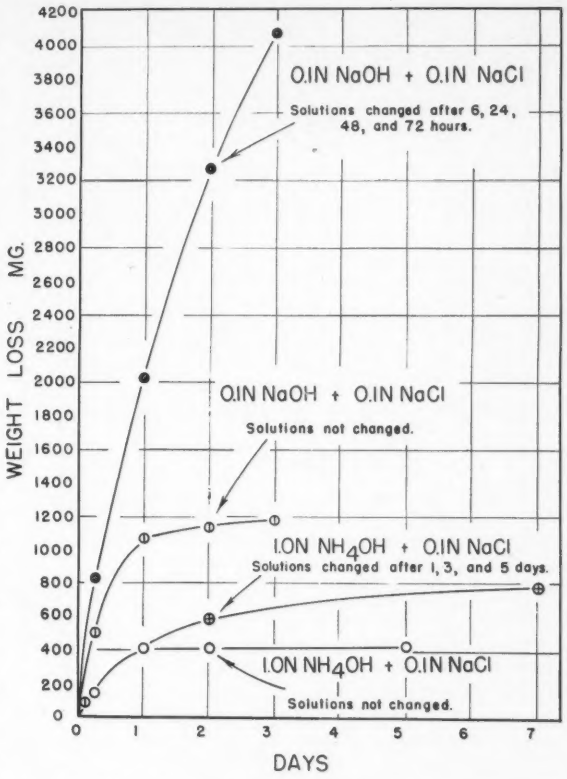

Figure 2—Effect of exposure time on weight loss on aluminum (2S-1/2H). Specimens exposed in hydroxide and ammonium hydroxide solutions.

The corrosion rate for ammonium hydroxide solutions was found to decrease very rapidly with time (Figure 2). In order to obtain corrosion rates representative of long time exposure periods, the rates of corrosion in ammonium hydroxide solution must be calculated from weight losses which occur after the attack has become fairly constant. It was found that the greatest part of the corrosion of an aluminum specimen in ammonium hydroxide solution occurs during the first 48 hours. Therefore, weight losses in ammonium hydroxide solutions were determined after two days and after seven days, and the calculated

*Commercial purity aluminum containing silicon 0.08%, iron 0.68%, copper 0.18%.

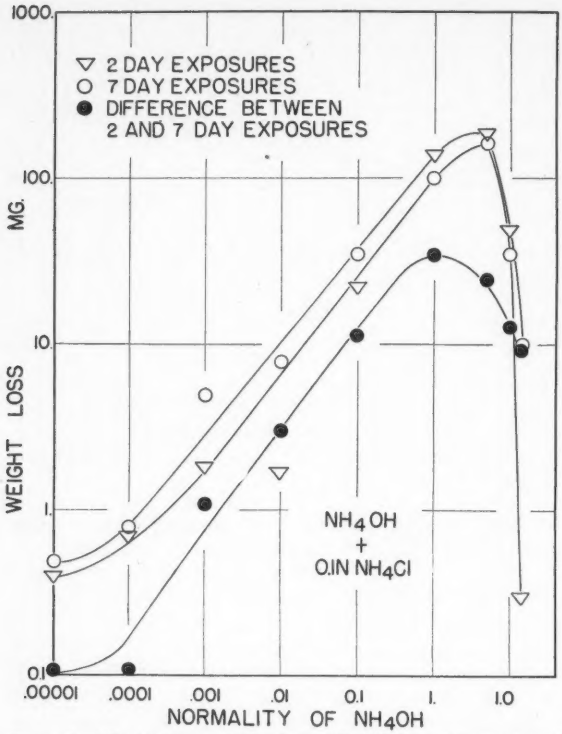

Figure 3—Weight losses of aluminum (2S-1/2H) specimens exposed in ammonium hydroxide solutions containing 0.1 normal ammonium chloride. Log-log plot.

penetration rate was based on the difference between the two-day and the seven-day weight losses.

Figure 3 shows the method used in obtaining the five-day weight loss curve which was used for calculating the corrosion rates of aluminum in ammonium hydroxide solutions containing 0.1 normal ammonium chloride. All of the other ammonium hydroxide solutions containing various salts were handled in a similar manner.

It was also found that for certain solutions, such as ammonium hydroxide and hydrochloric acid the rate of corrosion varied widely as a result of changing the ratio of the area of the specimen (sq cm) to volume of solution (cc); other solutions such as sulfuric and phosphoric acids were not appreciably affected by the variation of the area-to-volume ratio. The effect of area-to-volume ratios from 0.0025 to 0.168 on the rate of corrosion of aluminum in 1.0 normal phosphoric acid and 0.1 normal hydrochloric acid is shown in Figure 4, and in 3.0 normal ammonium hydroxide solutions in Figure 5. As explained above, the rate of penetration in ammonium hydroxide solutions is calculated from the difference between two-day and seven-day weight loss data.

In this work, a special effort was made to handle all the tests by an identical procedure. Therefore, the following program was closely adhered to. Specimens of commercial purity aluminum 0.064-inch by 0.5-inch by 4.0 inches were degreased in acetone and dried prior to weighing. Then the specimens were exposed in 500cc of solution, resulting in an area-to-volume ratio of 0.05 square centimeter per cc. Except for the "time versus weight loss" tests

and the seven-day ammonium hydroxide tests, all specimens were exposed for two days, and the solutions were changed after 24 hours. The specimens were exposed in quiescent solutions at room temperature.

During exposure, the tops of the beakers were covered with aluminum foil by crimping the foil tightly around the rim of the beakers. After exposure, the specimens were cleaned in chromic - phosphoric acid (2 percent CrO_3 and 5 percent H_3PO_4 by weight) at 80° C. for 10 minutes, to remove any corrosion product which had accumulated during exposure. When necessary, additional cleaning periods were used until the specimens were free of corrosion product. Corrosion data were based on the total weight losses. The pH was determined on the original solutions and on the solutions after exposure.

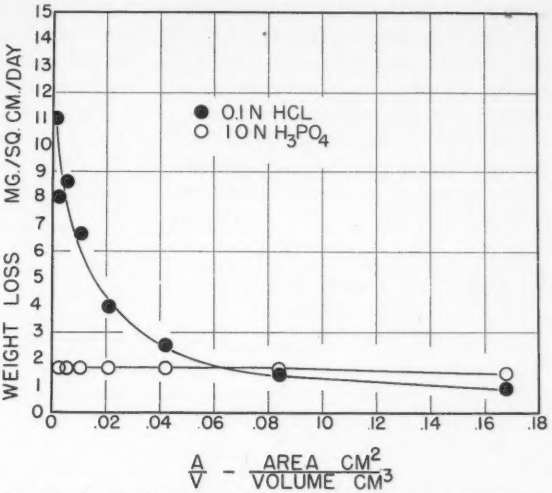

Figure 4—Effect of various area-to-volume ratios on rate of corrosion of aluminum (2S-1/2H) specimens exposed seven days in 0.1 normal hydrochloric acid and 1.0 normal phosphoric acid solutions.

These tests were conducted with solutions whose normalities ranged from 0.00001 normal to 0.1 normal with the intermediate concentrations increasing by tenfold. Exceptions to this procedure were the sodium carbonate and phosphoric acid tests which included 1.0 normal solutions and also the acetic acid and ammonium hydroxide tests which had concentrations increasing up to the highest available strength.

Aluminum is resistant to all concentrations of acetic acid, the greatest rates of attack being encountered in dilute solutions having a concentration in the neighborhood of 0.01 normal, as shown in Figure 6. Acetic acid solutions free of salt have very low rates of attack (less than 0.05 mils/year) at 0.00001 normal concentration. However, the rate increases sharply to about 4.0 mils/year at 0.01 normal, drops off gradually to about 1.3 mils/year at 10 normal, and then falls off sharply to about 0.2 mils/year in glacial acetic acid. The effect of 0.1 normal sodium acetate and 0.1 normal ammonium acetate additions is practically identical. The maximum rate is lowered slightly by the addition of these salts, but the peak still falls at 0.01 normal. When the concentration of sodium acetate is increased to 1.0 normal, the corrosion curve flattens out considerably.

More specifically, the rate of attack of acid solutions containing 1.0 normal sodium acetate falls between 0.4 to 0.8 mils/year over the entire range from 0.00001 normal up to glacial acetic acid. These low rates of attack indicate why aluminum is so successfully used for storage and for shipment of glacial acetic acid.

Effect of Sodium, Ammonium, and Phosphate Ions in Phosphoric Acid Solutions

The effect of phosphoric acid with and without the addition of di-sodium phosphate or di-ammonium phosphate* on the rate of corrosion of aluminum is shown in Figure 7. In the absence of sodium or ammonium salts of this acid, aluminum is relatively resistant to solutions up to 0.01 normal, the corrosion rate being about 5.0 mils/year** at this concentration. In the presence of either 0.1 normal di-sodium phosphate or di-ammonium phosphate aluminum is even more resistant and in solutions up to 0.2 normal phosphoric acid the rate of corrosion does not exceed 5.0 mils/year.

The effect of 1.0 normal di-sodium phosphate is not materially different from 0.1 normal concentrations of this salt except at concentrations of phosphoric acid lower than 0.001 normal where the rate is increased slightly, but this is of little practical significance.

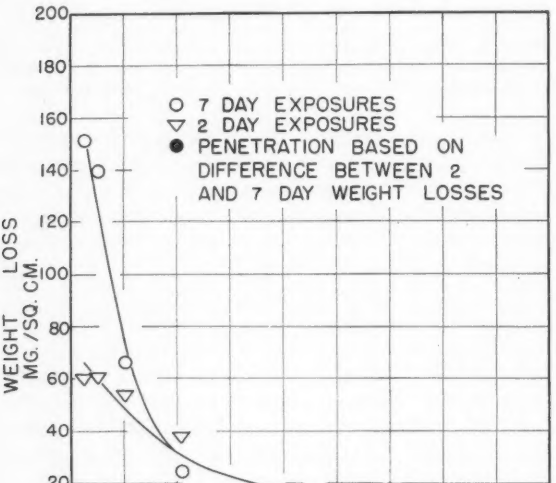

Figure 5—Effect of various area-to-volume ratios on rate of corrosion of aluminum (2S-1/2H) specimens exposed to 3.0 normal ammonium hydroxide solutions.

Effect of Sodium, Ammonium, and Sulfate Ions in Sulfuric Acid Solutions

For practical applications, aluminum can be used with sulfuric acid solutions up to 0.001 normal, although dilute sulfuric acid is somewhat more corrosive than phosphoric acid. The rate of corrosion in sulfuric acid appears to be fairly constant at

* The normality of a di-sodium or di-ammonium phosphate is based on the equivalents of sodium or ammonium ion.

** Throughout discussion 5 mils/year is used as criterion of resistance to corrosion. Below 5 mils/year is good resistance and above 5 mils/year is poor resistance to attack.

any given concentration regardless of the presence of 0.1 normal or 1.0 normal sodium or ammonium sulfate (see Figure 8). Apparently these salts neither accelerate nor inhibit the attack on aluminum by sulfuric acid.

Effect of Sodium, Ammonium, and Nitrate Ions in Nitric Acid Solutions

The resistance to corrosion of aluminum in dilute nitric acid is comparable to that obtained in dilute sulfuric acid solutions. However, the mechanism differs in that hydrogen is evolved in the case of sulfuric acid whereas in the case of nitric acid there is no hydrogen evolution. As seen in Figure 9, ammonium salt accelerates the attack to a greater extent than does neutral sodium salt. The curve for nitric acid containing 0.1 normal sodium nitrate is for all practical purposes the same as for nitric acid alone. On the other hand, while the curve for nitric acid plus 0.1 normal ammonium nitrate almost coincides at 0.00001 normal with the nitric acid curve, the corrosion rate of the former increases more rapidly as the corrosion of the acid increases until the attack becomes two to three times greater at concentrations of 0.001 to 0.1 normal nitric acid. The effect of 1.0 normal sodium nitrate and 0.1 normal ammonium nitrate is similar. A concentration of 1.0 normal ammonium nitrate causes about fivefold increases in the corrosion rate of aluminum in nitric acid solutions between the range of 0.00001 to 0.1 normal.

Effect of Sodium, Ammonium, and Chloride Ions in Hydrochloric Acid Solutions

Although hydrochloric acid is normally considered as being corrosive to aluminum, metal of commercial purity (2S-1/2H) is relatively resist-

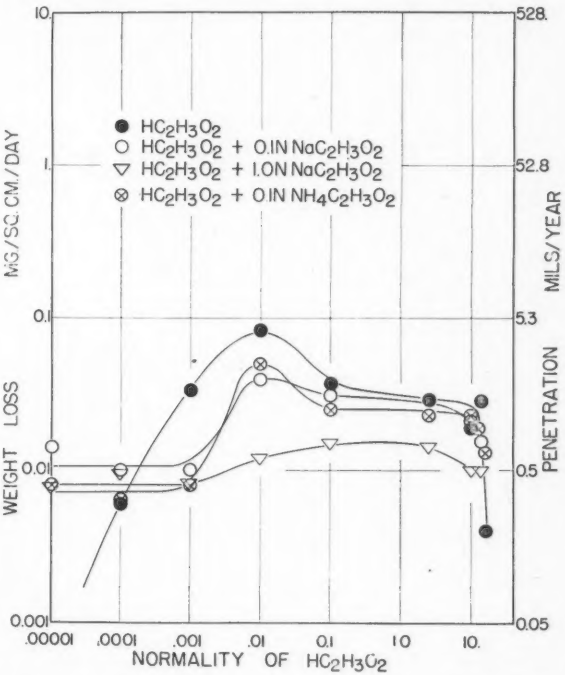

Figure 6—Effect of sodium, ammonium, and acetate ions in acetic acid solutions on rate of corrosion of aluminum (2S-1/2H). Log-log plot.

ant to solutions up to 0.001 normal. Figure 10 shows the effect of 0.1 and 1.0 normal sodium and ammonium chloride additions to hydrochloric acid solutions ranging in concentrations from 0.00001 to 0.1 normal. Plotted on log-log coordinates, the corrosion rate of commercial purity aluminum in hydrochloric acid solutions containing no salt varies linearly with the concentration. The addition of 0.1 normal sodium chloride or 0.1 normal ammonium chloride increases the attack slightly (about 25 to 50 percent), but of the two, ammonium chloride appears to cause slightly greater corrosion. The corrosion rate in 0.1 normal hydrochloric acid solutions increases very markedly (thirty-five to fortyfold) on the addition of 1.0 normal sodium or ammonium chloride. However, in the more dilute solutions below 0.01 normal hydrochloric acid, the increase is much smaller. It would be expected that ammonium chloride would cause somewhat greater corrosion than sodium chloride at the same concentrations, since ammonium chloride hydrolyzes to a greater extent and would therefore tend to increase the acidity of dilute hydrochloric acid solutions.

Effect of Ammonium, Chloride, Nitrate, Carbonate, Sulphate Acetate, and Chromate Ions in Ammonium Hydroxide Solutions

Not all alkaline solutions cause

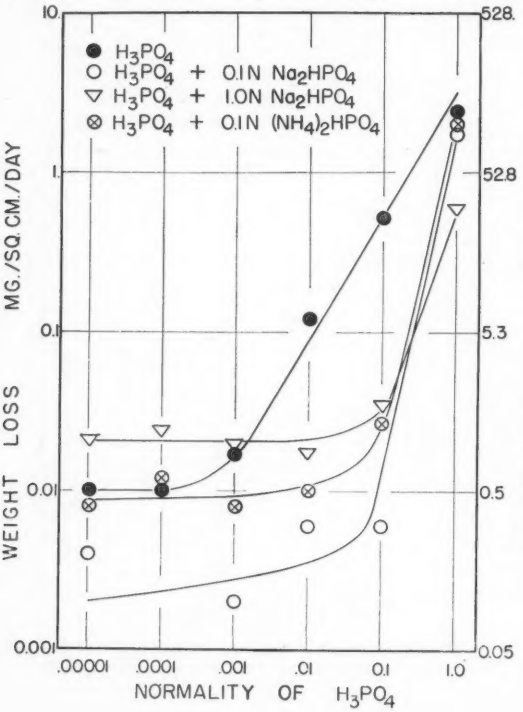

Figure 7—Effect of sodium, ammonium, and phosphate ions in phosphoric acid solutions on rate of corrosion of aluminum (2S-1/2H). Log-log plot.

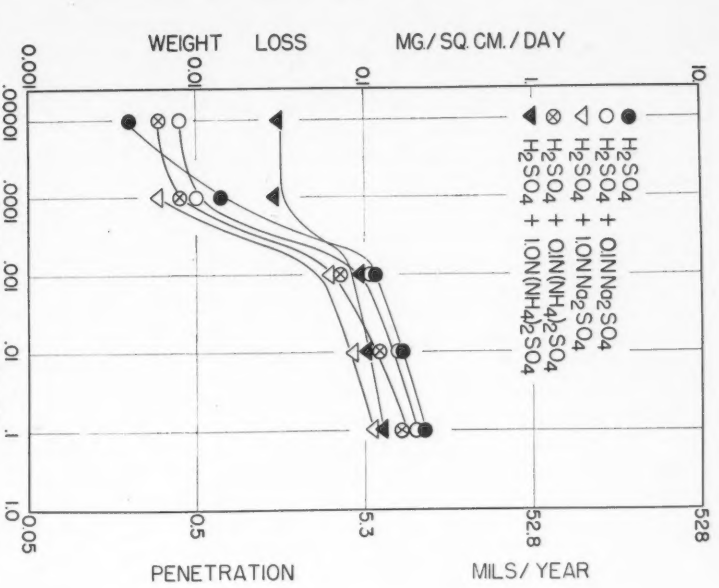

Figure 8—Effect of sodium, ammonium, and sulfate ions in sulfuric acid solutions on rate of corrosion of aluminum (2S-1/2H). Log-log plot.

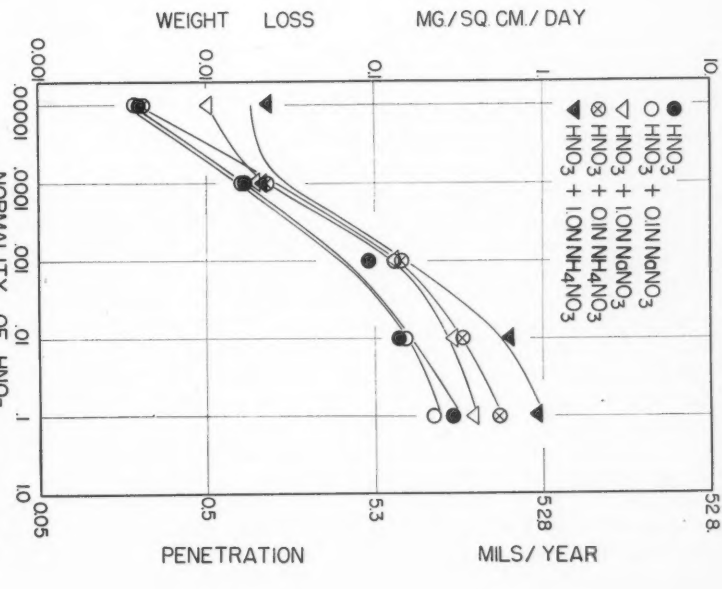

Figure 9—Effect of sodium, ammonium, and nitrate ions in nitric acid solutions on rate of corrosion of aluminum (2S-1/2H). Log-log plot.

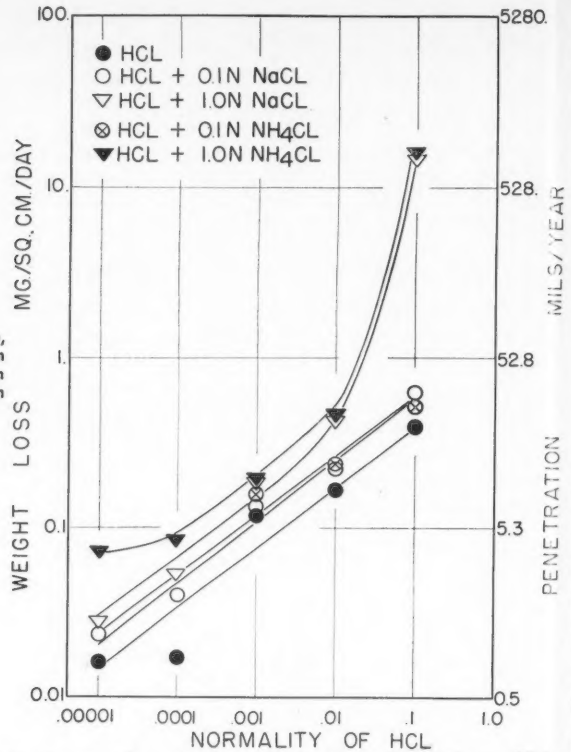

Figure 10—Effect of sodium, ammonium, and chloride ions in hydrochloric acid solutions on rate of corrosion of aluminum (2S-1/2H). Log-log plot.

rapid corrosion of aluminum as evidenced by the fact that many ammoniacal solutions such as ammonium hydroxide can be handled in aluminum equipment. It appears that for ammonium hydroxide solutions, the ions present in a particular solution have a greater influence on the rate of corrosion than does the concentration of the ammonium hydroxide. It is significant to note that whereas the corrosion rate of aluminum is sodium hydroxide solution increases as the concentration increases, the rate in ammonium hydroxide solution increases to a maximum at a concentration of 1.0 to 5.0 normal and then decreases as the concentration is increased further. This wide difference in corrosion rates in sodium hydroxide and ammonium hydroxide solutions is undoubtedly closely related to the solubility of the corrosion products in the two solutions.

The effect of ammonium chloride on the rate of corrosion of aluminum in ammonium hydroxide is shown in Figure 11. The rate of corrosion of aluminum in amomnium hydroxide solutions which are free of salt increases gradually from a rate of 0.07 mils/year at 0.00001 normal to a maximum of 10 mils/year at 5.0 normal and then decreases to 3.4 mils/year at 14.8 normal. Below 0.1

normal ammonium hydroxide the attack is reduced by 0.1 normal ammonium chloride. Above 0.1 normal ammonium hydroxide the attack is not materially affected by the presence of 0.1 normal ammonium chloride. With 1.0 normal ammonium chloride the reverse is true, i. e., the attack is accelerated slightly in dilute solutions less than 0.001 normal, but decreased in solutions above 5.0 normal. The maximum rate of attack is of the same order of magnitude either with or without the ammonium chloride and falls between 1.0 to 5.0 normal.

The addition of ammonium nitrate to ammonium hydroxide solutions diminishes the rate of attack at all concentrations except 1.0 normal, the point of maximum attack. The ability of 1.0 normal ammonium nitrate to reduce the rate of corrosion is slightly greater than for 0.1 normal, (see Figure 12).

Ammonium carbonate is effective in decreasing the corrosion by ammonium hydroxide, as can be seen in Figure 13. With 0.1 normal ammonium carbonate the rate of corrosion is held costant at 0.6 mills/year for concentration of ammonium hydroxide up to 0.01 normal. Above this concentration the rate accelerates to a maximum of 10 mils/year at 5.0 normal ammonium hydroxide. This maximum is the same as for ammonium hydroxide solutions containing no salt. Further increase in the concentration of ammonium hydroxide causes the rate of corrosion to drop to 0.2 mils/year at 14.8 nor-

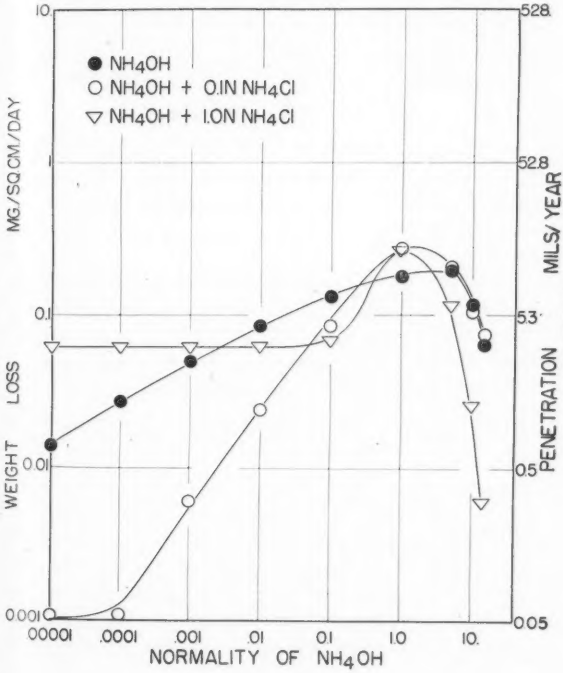

Figure 11—Effect of ammonium and chloride ions in ammonium hydroxide solutions on rate of corrosion of aluminum (2S-1/2H). Log-log plot.

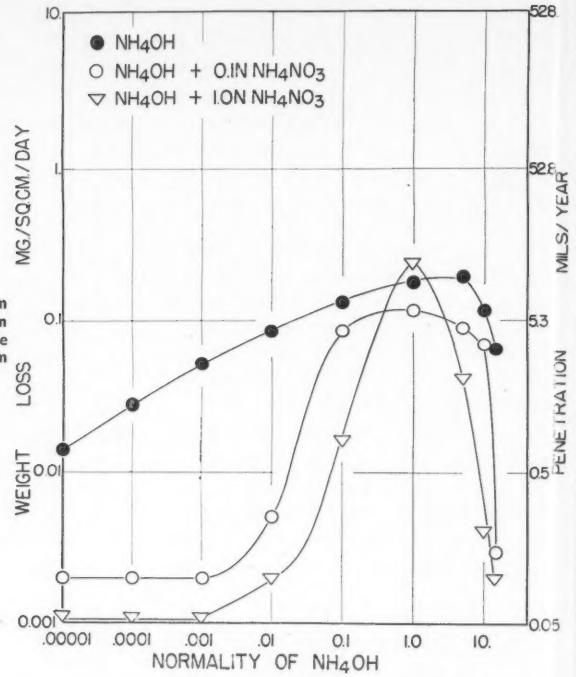

Figure 12—Effect of ammonium and nitrate ions in ammounium hydroxide solutions on rate of corrosion of aluminum (2S-1/2H). Log-log plot.

mal. The presence of 1.0 normal ammonium carbonate causes an even greater reduction of corrosion at all concentrations of ammonium hydroxide, the rate being constant at 0.05 mils/year for concentrations up to 0.1 normal. The rate then increases to a maximum of 1.3 mils/year at 5.0 normal and then drops to 0.05 mils/year at 14.8 normal.

The effect of ammonium acetate on the rate of corrosion was found to be quite similar to ammonium chloride and ammonium nitrate additions to ammonium hydroxide. The presence of ammonium chromate was found to hold the corrosion rate at 0.1 mils/year regardless of the concentration of ammonium hydroxide.

Effect of Sodium, Chloride, Sulfate, Nitrate, Acetate, and Chromate Ions in Sodium Hydroxide Solutions

Because the hydrated oxides of aluminum are amphoteric it was anticipated that aluminum would be rapidly attacked by alkaline solutions. As has been shown in Figures 1 to 13, inclusive, aluminum is resistant to solutions made alkaline by ammonia. Although alkalinity produced by the presence of sodium hydroxide (Figure 14) or resulting from hydrolysis of a sodium salt such as the carbonate (Figure 16) causes appreciable corrosion, aluminum may or may not be resistant

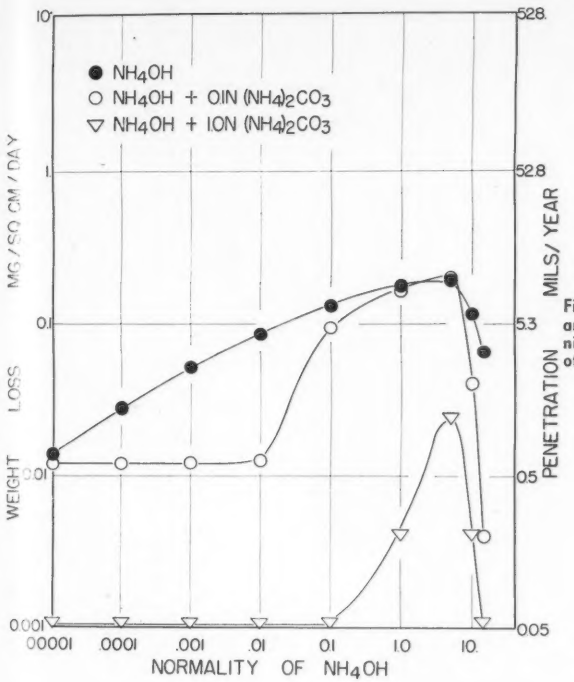

Figure 13—Effect of ammonium and carbonate ions in ammonium hydroxide solutions on rate of corrosion of aluminum (2S-1/2H). Log-log plot.

to such solutions, depending upon the nature of other ions present.

The addition of 0.1 normal sodium chloride to sodium hydroxide solutions has very little effect on the rate of corrosion. However, the addition of 1.0 normal sodium chloride tends to produce slightly lower rates of attack in more concentrated sodium hydroxide solutions and slightly higher rates in dilute solutions. The effect of sodium sulfate, sodium nitrate, and sodium acetate on the rate of corrosion of aluminum in sodium hydroxide solutions is entirely analogous to that of sodium chloride in sodium hydroxide solutions. Because of the fact that the corrosion curves for the above salts in sodium hydroxide are not significantly different, only the curves for sodium hydroxide containing sodium chloride are shown. However, aluminum is very resistant to solutions which may be as high as 0.01 and 0.1 normal in sodium hydroxide if they are 0.1 and 1.0 normal, respectively, in sodium chromate* (Figure 15).

Discussion

In many neutral solutions, the corrosion of structural metals is closely associated with the flow of current between the anodic areas and the cathodic areas on the metal.

* The normality of sodium chromate is based on the equivalent of sodium ion.

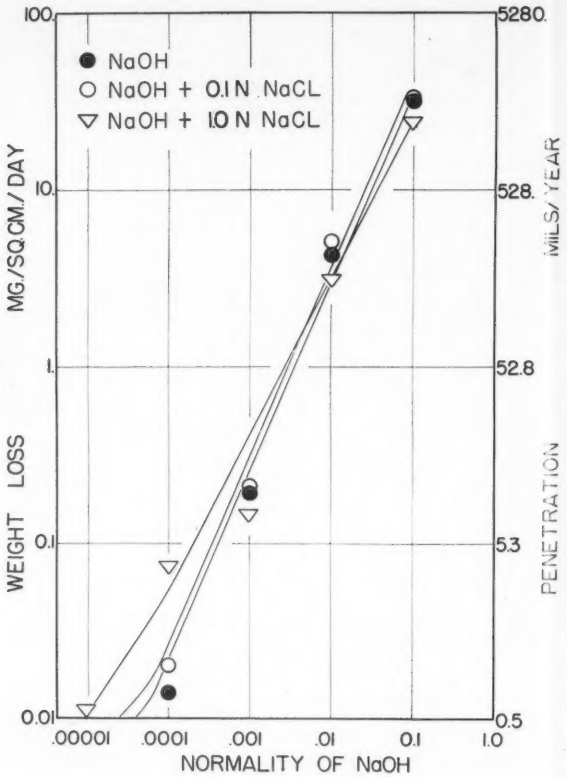

Figure 14—Effect of sodium and chloride ions in sodium hydroxide solutions on rate of corrosion of aluminum (2S-1/2H). Log-log plot.

There is considerable quantitative evidence to show that for aluminum there is a direct correlation between the quantities of current flowing between the anodic and cathodic areas and the weight of metal dissolved.[4] Since the quantity of metal dissolved is directly related to the flow of current, it logically follows that the extent of corrosion is influenced considerably by the polarization characteristics of the anodic and cathodic areas and by the conductivity of the solution.

In hydrochloric acid solutions, the rate of corrosion increases as the concentration increases. Two factors contribute to this increase in the rate of attack. First, the greater hydrogen ion activity decreases the stability of the oxide film and also increases the solubility of the corrosion products. Second, the increase in concentration results in solutions having greater conductivities. Since the resistance offered by more concentrated solutions to the flow of current is less than in dilute solutions, more current flows from the anodic areas to the cathodic areas, and therefore more metal goes into solution. For a given concentration

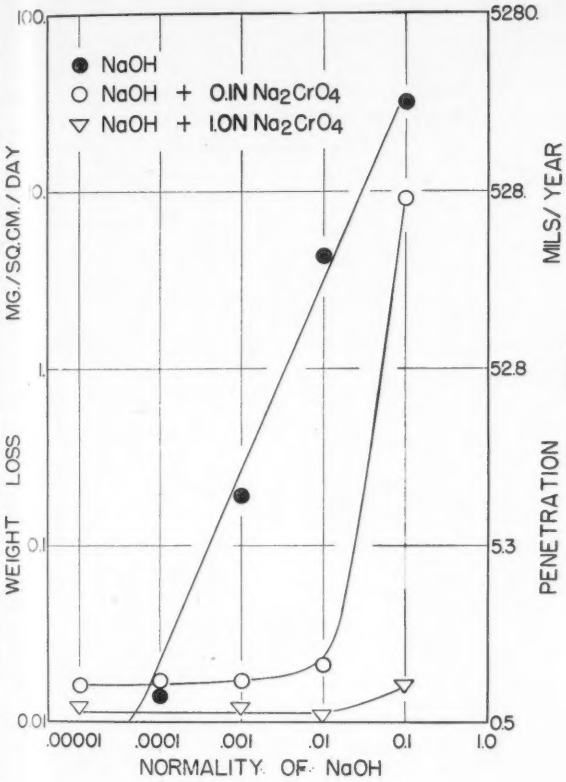

Figure 15 — Effect of sodium and chromate ions in sodium hydroxide solutions on rate of corrosion of aluminum (2S-1/2H) Log-log plot.

of hydrochloric acid, the addition of either sodium chloride or ammonium chloride increases the rate of corrosion. By the addition of either of these salts, the conductivity is increased, which would be expected to cause an increase in the amount of corrosion. The ammonium cation appears to be slightly more corrosive than the sodium cation because ammonium chloride hydrolyzes (to form HCl) to a greater extent than does sodium chloride.

Corrosion rates in sulfuric acid solutions proved to be lower than the rates in hydrochloric acid solutions. This condition is partly explained by the greater penetrating power of the chloride anion. The difference in corrosion rates is further clarified by an understanding of the character of the polarization curves in the presence of chlorides and sulfates.[4] In the presence of chloride ion there is very little anodic polarization of aluminum. Consequently, a greater quantity of current flows and produces correspondingly greater corrosion. However, in sulfate solutions aluminum polarizes anodically to an appreciable extent. Since the total cur-

rent flow is decreased, the extent of the corrosion must also be lower.

The greatest rates of corrosion were encountered in sodium hydroxide solutions. The extremely high solubility of the corrosion products contributes much to the high rates of attack.

In direct contrast to sodium hydroxide solutions, low rates of attack were obtained with ammonium hydroxide solutions. This wide difference in corrosion rates in two different alkaline solutions can be explained by the great difference in the solubility of the corrosion product in the two solutions.

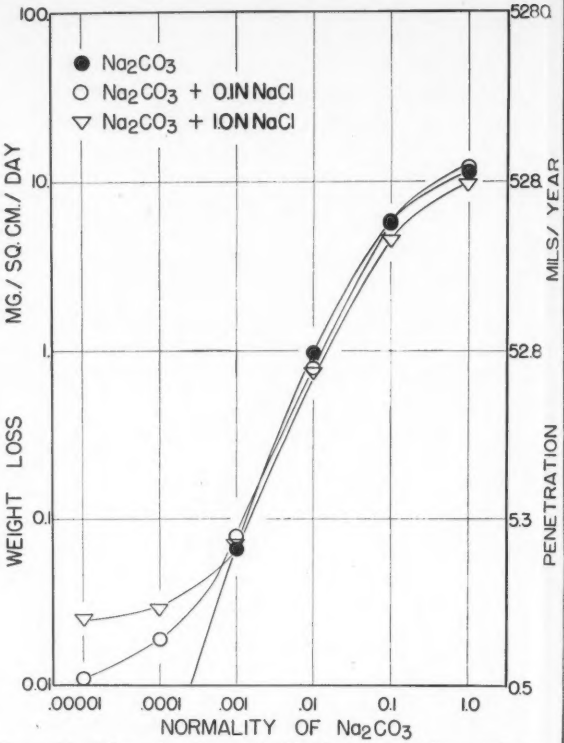

Figure 16—Effect of sodium and chloride ions in sodium carbonate solutions on rate of corrosion of aluminum (2S-1/2H). Log-log plot.

Archibald and Habasian[5] obtained some data on the solubility of aluminum hydroxide in ammonium hydroxide solutions. These data are shown graphically in Figure 17. This solubility versus concentration curve is strikingly similar to the corrosion curves for aluminum in ammonium hydroxide solutions. Both curves pass through a maximum. Also shown in Figure 17 is the effect on the solubility of aluminum hydroxide caused by potassium and ammonium cations and by nitrate anions. These ions were added in various concentrations as potassium nitrate and ammonium nitrate.

It is evident that the solubility of aluminum hydroxide increases as the concentration of potassium nitrate increases, and decreases as the amount of ammonium nitrate increases. It would be expected that salts such as sodium chloride, sodium nitrate, sodium sulfate, etc., would behave similarly to potassium nitrate and that salts such as ammonium chloride, ammonium acetate, ammonium carbonate, ammonium sulfate, etc., would behave similarly to ammonium nitrate.

Conclusions

From these beaker-type corrosion tests at room temperature it may be concluded that:

1) Aluminum is resistant to corrosion by acetic acid solutions, both in the presence and in the absence of sodium or ammonium salts of this acid.

2) Aluminum is resistant to corrosion by mineral acids in concentrations up to 0.001 normal, either in the presence or in the absence of sodium or ammonium salts of the corresponding acids.

3) Aluminum is resistant to corrosion by phosphoric acid in concentrations up to 0.01 normal. In the presence of sodium or ammonium salts of this acid, aluminum is resistant to corrosion in concentrations up to 0.2 normal phosphoric acid.

4) In acid solutions containing only one anion, the corrosion rate increases in this order: acetate, phosphate, sulfate, nitrate, and chloride.

5) Aluminum is resistant to corrosion by ammonium hydroxide, both in the presence and in the absence of chloride, nitrate, carbonate, acetate, sulfate, and chromate salts of ammonia.

6) Aluminum is significantly attacked in concentrations of sodium hydroxide above 0.0005 normal, either in the presence or in the absence of chloride, sulfate, nitrate, and acetate salts of sodium.

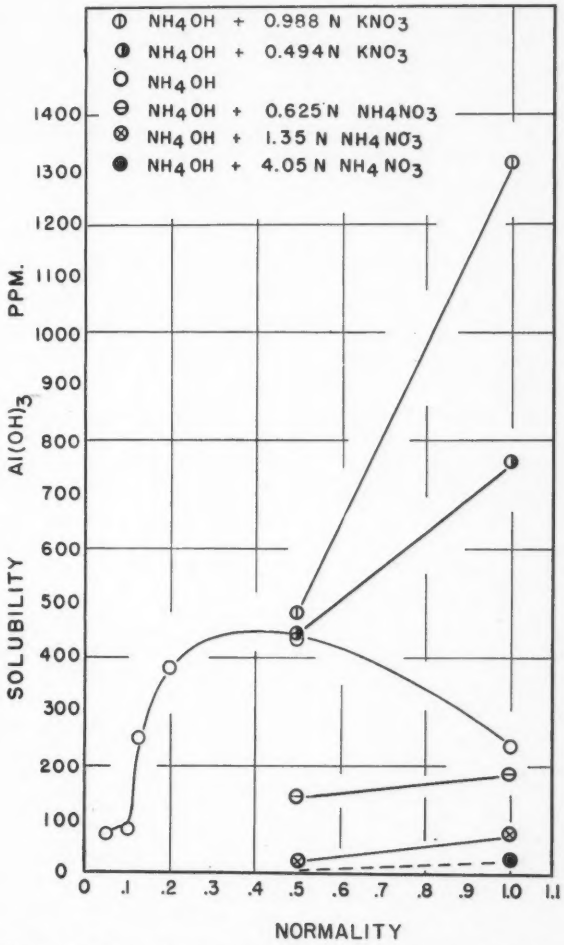

Figure 17—Effect of potassium nitrate and ammonium nitrate on the solubility of aluminum hydroxide in ammonium hydroxide. (Reference 5).

7) Aluminum is resistant to dilute (less than 0.1 normal) sodium hydroxide solutions containing chromate anion at a concentration of 1.0 normal.

8) The sodium salts of chloride, nitrate, sulfate, and acetate anions do not affect the action of sodium hydroxide on aluminum. The chromate anion definitely retards the action of sodium hydroxide on aluminum.

9) Aluminum is resistant to sodium carbonate solutions up to 0.001 normal concentrations, either in the presence or in the absence of sodium chloride, but in higher concentrations, the behavior is similar to that in sodium hydroxide solutions.

10) The resistance to corrosion of aluminum appears to be influenced to an appreciable extent by the stability of the oxide film and by the solubility of the corrosion product.

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Thermogalvanic Corrosion II*

*By R. M. Buffington**

THIS ARTICLE is a continuation of the discussion of thermogalvanic corrosion presented by N. E. Berry[1] at the 1946 Kansas City meeting of the National Association of Corrosion Engineers and which was subsequently reproduced in the Association journal, CORROSION.

Thermogalvanic corrosion is a form of galvanic action in which metal is removed from one surface and deposited on another as a result of a temperature difference between the two. The electrode reactions are the reverse of each other; the oxidizing agent which is reduced at the cathode is regenerated at the anode. Therefore thermogalvanic corrosion can continue indefinitely without any new supply of oxidizing agent, at a rate limited by that at which the regenerated supply can reach the cathode.

Here we will deal with the subject from a thermodynamic and physicochemical point of view. A test is described whereby it is shown that under certain conditions, which can readily be recognized experimentally, the standard thermodynamic relations for reversible systems apply to the open-circuit potentials of thermogalvanic cells, in spite of the fact that overall temperature equilibrium is not established. The significance of thermogalvanic data in connection with the thermodynamics of electrolytic solutions is discussed. A simple equation [16] is developed for calculating standard values of the temperature coefficients of thermogalvanic potentials and therefore the potentials themselves, from readily available data. Standard coefficients so calculated are given for a number of electrode reactions in Table II.

Reversibility of Open-Circuit Potentials

Thermodynamic treatments of systems which are not in temperature equilibrium are as a rule complicated by non-thermodynamic factors and not very convincing. In certain cases, however, notably that of metallic thermocouples, it can be shown that the process in question is reproducible and reversible in spite of irreversible processes which go on independently. In such cases the non-thermodynamic factors do not enter, and the standard thermodynamic relations of reversible processes apply. The question is

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* Research Department, Servel, Inc., Evansville, Indiana.

whether and under what circumstances this is true of thermogalvanic cells. The first step will be to review the evidence in the closely related case of metallic thermocouples.

Thermocouples

Ohm's Law applies, without complications from polarization or other effects, to the isothermal conduction of electricity through two dissimilar metals in series. At sufficiently small currents, the potential drop becomes negligible and conduction therefore becomes reversible and with it the thermoelectric Peltier absorption or evolution of heat which accompanies the flow of current across the junction. The conditions are exactly those which apply to the junctions and isothermal portions of a thermocouple during open-circuit, i.e., potentiometric, measurements of its potential.

The reversible transfer of heat from higher to lower temperatures by Peltier effects of opposite sign at the two junctions produces work, and thus is responsible for part of the open-circuit potential; the rest comes from Thomson evolution and absorption of heat which occurs as the current passes through the temperature gradients in the two metals in opposite directions. The remaining question is whether the Thomson or gradient contribution is reproducible for fixed values of the junction temperatures, or whether it varies with the temperature distribution in the couple and thus is in some degree linked with irreversible heat conduction and heat exchange with the surroundings.

The experimental answer can be observed in connection with the well-known loop test for uniformity of thermocouple wire, in which a wire is pulled through hot kerosene while its ends are at the same temperature and connected to a galvanometer. A large and highly unsymmetrical temperature hump is thus moved along the wire. Small random variations in potential are produced as thermoelectric irregularities pass through the temperature hump, but no systematic potential in a single direction. This shows that the Thomson potentials of the two equal and opposed temperature differences in the same metal cancel each other, even when one temperature gradient is much steeper than the other. This is certainly true for various kinds of commercial thermocouple wire, both pure metals and alloys, and presumably is true for metallic conductors in general.

Together, the isothermal and non-isothermal tests cover the entire thermocouple. From them it follows that aside from effects of non-uniformities, which have nothing to do with the present subject, the open-circuit potential of a metallic thermocouple is reproducible for given junction temperatures and is to be ascribed to a definite reversible *ther-*

TABLE I

Relative entropy of chloride ion at 15° C. in 0.01 M solutions of various chlorides, referred to that of conducting electrons in mercury as zero.

	S'_{Cl^-} e.u.; cal./mol/°C
HCl—Hydrochloric Acid	20.6
LiCl—Lithium Chloride	28.5
NaCl—Sodium Chloride	27.3
KCl—Potassium Chloride	27.1
RbCl—Rubidium Chloride	27.0
NH_4Cl—Ammonium Chloride	28.5
Average, excluding HCl—Hydrogen Chloride	27.7

mocouple process proper, which consists of electrical conduction and the associated Peltier and Thomson processes. The same conclusions follow from direct tests of the reproducibility of thermocouple potentials but with a larger margin for possible error.

Thermogalvanic Cells

In a thermogalvanic cell, one of the two metallic elements of a thermocouple is replaced by an electrolytically conducting solution, and metallic conduction across the junctions is replaced by anodic oxidation and the reverse cathodic reduction. Passage of current is accompanied by Peltier and Thomson transfer of heat, at the electrodes and in the temperature gradients, respectively, and by transfer of electrode material and of ions from one electrode temperature to the other. The problem of determining in specific cases whether measured open-current potentials are reversible, apparently is as follows. There are three steps to be considered. The metallic-conduction step has been already shown to be reversible. The electrode reaction may or may not be reversible; isothermal tests suffice to determine whether it is. Given a reversible electrode reaction, the electrolytic-conduction step can be tested using the same principle as for metallic conduction. A Cu-Cu^{++} cell, Table II., was chosen, for test.

The first step is to identify electrode reactions with which later tests are to deal, and to prove that high and low temperature reactions are the reverse of each other. This sometimes may be a difficult matter; an expected reaction may fail to occur, and some other reaction may carry sufficient current to permit the measurement of open-circuit potentials, and may behave reversibly. In this particular case, evidence that the electrode equilibria are between Cu and Cu^{++} as assumed is as follows: In previous tests with such cells, short-circuiting the electrodes caused metallic copper to plate from the cold anode to the hot cathode, and no other products were visible at either electrode. (But when neutral $CuSO_4$ (copper sulfate) solution was used, basic sulfates formed on a steam-heated electrode.) $CuSO_4$ supplies the dissolved copper as Cu^{++}; furthermore, it is well known that Cu^{+} is unstable with respect to Cu and Cu^{++} in such a solution, and that the electrochemical equivalent of copper as determined by plating tests corresponds to Cu^{++} and not to Cu^{+}.

Design of Cell

Figure 1 shows a Cu-Cu^{++} cell designed specifically for reversibility tests. The cell was filled with 0.1 molar copper sulfate, 0.05 molar sulfuric acid solution and allowed to

TABLE II.—Cu-Cu^{++} CELL

Anode	Solution	Cathode
Cu (at t)	(0.1 M $CuSO_4$, 0.05 M H_2SO_4)	Cu (at t + Δ t)
Anode reaction:	$Cu \rightarrow Cu^{++}$ (in soln.) + 2 e^- (in Cu)	
Cathode reaction:	Cu^{++} (in soln.) + 2 e^- (in Cu) $\rightarrow$ Cu	

stand at room temperature for several hours with occasional mixing, in order to convert traces of copper oxide and oxygen into their Cu^{++} equivalents and equalize the Cu^{++} concentration. Once the preliminary equilibration was complete, the cell potential did not vary from zero by more than 0.3 millivolt. The variations were apparently thermogalvanic and due to fluctuations in the electrode temperatures; in any case, they were small in comparison with the thermogalvanic potential of about 75 millivolts which is obtained between steam and cooling-water temperatures. Changes in potential of 0.1 millivolt were sufficient to reverse the direction of the galvanometer deflection and therefore of the current through the cell. Polarization potentials developed as current passed, but not fast enough to affect normal open-circuit potential measurements. These results confirm those obtained in the regular course of thermogalvanic measurements on other Cu-Cu^{++} cells with similar solution composition, and constitute direct proof of the reversibility of the electrode reactions, and of all processes which are thermodynamically linked with the passage of current through the cell, at a uniform temperature and with very small values of the current. It was not considered necesary to re-

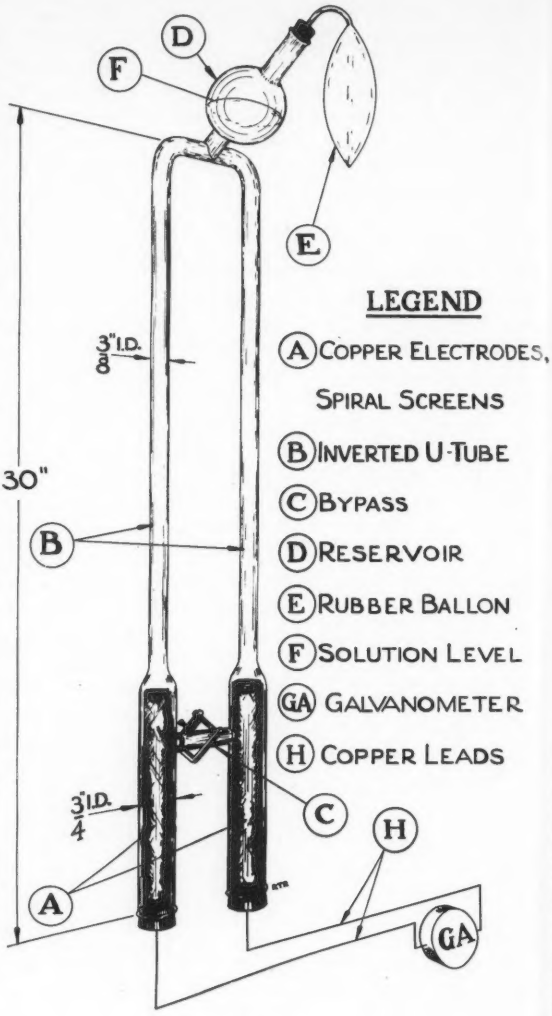

Figure 1

peat these tests at steam temperature, in view of previous experience which showed satisfactory electrode behavior.

Having proved that the electrodes operated reversibly and that the potential between them did not exceed 0.3 millivolt with the whole cell at approximately the temperature of the room, the reversibility of electrolytic conduction was tested by setting up an unsymmetrical temperature hump in a portion of the electrolytic path while watching the galvanometer for deflections. A flame was applied with by-pass C closed, and the temperature of the solution was raised almost to the boiling point in the horizontal part of the inverted U-tube, and tapered off gradually in one side-tube, leaving the gradient steep on the other. Heating of the electrodes and spreading of the steep gradient were avoided in the design, which prevented general circulation, and guarded against local thermal convection by placing the hotter, lighter solution on top. The potential variations were well within the 0.3 millivolt limit; no significant transient or persistent potentials were developed. The same was true when slight boiling occurred in the upper part of the hot leg, thus showing that rapid convection had no effect.

New Cell Arranged

The solution was then replaced by one containing 50 percent lithium bromide, 0.15 percent lithium hydroxide, and 0.10 percent cuprous bromide. In the new cell, electrode equilibrium is established between copper, bromide ion, and a complex cuprous bromide ion, probably $CuBr^-_3$. The effective internal resistance of this cell was much higher than that of the original cell, but no difficulty was found in making open-circuit potential measurements. The potentials of the two cells are about the same, but opposite in sign; copper plates from the hot to the cold surface through this solution and others in which the dissolved copper is present as a cuprous chloride or bromide complex ion. Both the isothermal and the unsymmetrical temperature hump tests were repeated, with essentially the same results as for the original cell.

Test Results

The results of the unsymmetrical temperature hump tests prove, within rather narrow limits of possible error, that electrolytic conduction through a temperature gradient is reversible under open-circuit conditions for two very different solutions of uniform composition. It is asumed that this will prove to be true in general for such solutions, and it is known to be true of metallic conduction. This means that all gradient processes which affect the thermogalvanic potential are reversible and independent of irreversible processes and therefore are completely determined by the electrode reaction and the temperatures of the electrodes.

It follows that the reversibility of the open-circuit potential of a thermogalvanic cell in which the solution is of uniform composition is determined solely by the reversibility of the electrode reaction, and further that standard thermodynamic relations for reversible processes apply to the electrode reac-

tion. No other reaction need be specifically considered. If it seems strange that it is not necessary to describe the electrolytic conduction through the gradient by the various ions present, the adequacy of the electrode reaction can be verified by "completing the cycle," that is, by adding to the actual cell process the processes necessary to restore the cell to its original condition.

Soret Effects

The above conclusions, which form the simplest possible basis for developing the thermodynamics of thermogalvanic cells, have not been generally accepted in the past because of a common suspicion that the electrode reaction does not tell the whole story, and that irreversible gradient processes affect the thermogalvanic potential. One frequently quoted reason for suspicion is the existence of thermal diffusion or "Soret" effects, whereby temperature differences tend to cause concentration differences to develop in an originally uniform solution. Of course, the potential would be changed if thermal diffusion were allowed to produce actual changes in concentration, but this is beside the point. The author can see no reason to expect a mere tendency for thermal diffusion to make the thermogalvanic potential dependent on the temperature distribution in the gradient, and believes electrolytic conduction to be reversible as assumed, regardless of the tendency for thermal diffusion.

From the experimental point of view, the question is straightforward. It can be determined by means of unsymmetrical temperature hump tests whether the electrolytic conduction step is reversible, and if it is, the standard thermodynamic relations apply. This is true in principle even if the electrode reactions are not actually reversible, as the reversible potential can be determined by means other than direct measurement.

The unsymmetrical temperature hump test is a test on the solution; the reversible electrodes are merely part of the apparatus, and it makes no difference which ones are used so long as they work. Likewise, the same electrodes can be used to test a variety of solutions, by varying the concentrations of the reactive ions and adding unreactive ions as desired.

With some modifications, the tests can be applied to thermogalvanic cells of a different type, in which the electrode reaction involves the solubility of a solid compound, for instance:

$$Hg + Cl^- \rightarrow HgCl + e^- \text{ in } Hg$$

Such cells are important from the theoretical point of view, as they greatly increase the number of ions which can be studied. Reversibility tests and actual potential measurements on such cells should be designed to avoid trouble from the change in solubility with temperature and to detect it if it occurs. Thus circulation should be minimized, and the solution should be brought to solubility equilibrium for a safe distance around each electrode. Unsymmetrical temperature hump tests should be made with the two electrodes at widely different fixed temperatures, so as to test the effect of the difference in concentrations. It is predicted that electrolytic conduction will prove to be reversible if the solubility of

the solid is low, but it is suspected that deviations may occur if the solubility is high and changes rapidly with the temperature.

Thermodynamic Relations

Gibbs-Helmholtz Equation

The application of the first and second laws of thermodynamics to reversible reactions is expressed in the well-known Gibbs-Helmholtz equation:

$$\frac{dE}{dT} = \left(\frac{\Delta S}{23054\ n}\right) = \left(\frac{\Delta H}{23054\ n} + E\right)\frac{1}{T} \qquad [1]$$

and its derivative:

$$\frac{d^2E}{dT^2} = \frac{1}{23054\ n}\frac{d\ \Delta\ S}{dT} = \frac{1}{23054\ n}\frac{\Delta\ C_p}{T} \qquad [2]$$

E is the reversible electromotive force in volts, at the absolute centigrade temperature T, for the reaction for which Δ S, Δ H, and Δ C_p are respectively the increases in entropy, heat content and specific heat. Δ H is in calories, and Δ S and Δ C_p in cal./°C, for the quantities in gram-mols indicated by the chemical equation as written; and n is the corresponding number of equivalents of oxidation or the number of Faradays of electricity passing through the cell. The nomenclature is essentially that of Lewis and Randall.[2]

Reactions in Cells

In an ordinary galvanic cell, two different half-reactions occur at the same temperature; in a thermogalvanic cell, the same half-reaction occurs in opposite directions at two different temperatures. For a reversible galvanic cell, the Gibbs-Helmholtz equation applies to the overall cell reaction, and to the anodic and cathodic half-reactions individually; for a reversible thermogalvanic cell, it applies to the half-reaction. Restating the results of the previous section, reversibility of a thermogalvanic cell means that the thermodynamics of the cell is that of the half-reaction. A given half-reaction has the same thermodynamics whether it occurs in a galvanic cell or a thermogalvanic cell. If reversible cells of both types involve the same identical half-reaction, data from the two types of cell can be combined on an additivity basis. That is, the dE/dT, Δ S, Δ H, etc., of a galvanic cell equal the sums of the corresponding quantities for the two corresponding thermogalvanic cells.

Consider a reversible thermogalvanic cell, composed of two identical electrodes of divalent metal M in a solution of uniform composition, containing M^{++} ions. Any metal might be chosen for the conductors which carry current through the temperature gradient outside the cell; copper will be specified. The half-reaction is then:

$$M \rightarrow M^{++}\ (\text{in soln.}) + 2\,e^-\ (\text{in Cu})$$

The corresponding Gibbs-Helmholtz equation is:

$$\Delta S = S_{M^{++}\ (\text{in soln.})} + {}^2S_{e^-\ (\text{in Cu})} - S_M = 2 \times 23054\ dE^*/dT \qquad [3]$$

The asterisk is used to identify thermogalvanic potentials. The convention is adopted of writing half-reactions in the anodic form, and of taking dE*/dT as positive if the higher temperature electrode is most anodic. Consistent with the above, E* is taken to be the thermogalvanic potential of the cell between a fixed temperature T_o and

a variable temperature T. Experimentally, dE*/dT is the slope of the E* vs T curve at a particular value of T. dE*/dT is independent of the choice of T_o, and E* has the same sign as dE*/dT if T is greater than T_o.

The quantity,

$$S_{M^{++}\text{ (in soln.)}} + {}^2S_{e^-\text{ (in Cu)}}$$

may be termed the relative entropy of M^{++} ions in the particular solution referred to that of conducting electrons in copper as zero, and denoted by the symbol $S'_{M^{++}}$. Then the Gibbs-Helmholtz equation may be written in the form:

$$S'_{M^{++}} = S_M + 2 \times 23054 \frac{dE^*}{dT} \qquad [4]$$

In this, and in other cases where only one ion enters into the half-reaction, the Gibbs-Helmholtz equation for a reversible thermogalvanic cell gives the relative entropy of the reactive ion in the particular solution used, referred to that of conducting electrons in an arbitrarily chosen standard metal as zero, in terms of experimentally measurable quantities, namely the absolute entropies of the electrode materials and the dE*/dT of the cell. Therefore, the relative entropies of the reactive ions can be determined experimentally, using the same scale-zero for all ions at all concentrations. The relation for more complicated half-reactions are not so direct, but are nevertheless useful.

The general utility of values of relative entropies of ions—on a different relative basis however—is well known among investigators in the general field of the thermodynamics of electrolytic solutions, chiefly through the work of Latimer[3] and his associates. Equation 4 suggests a very promising application of thermogalvanic methods in this field, to a systetmatic study of the effects of composition and concentration on ionic entropies: assuming that further unsymmetrical temperature hump tests turn out as predicted, and prove that a sufficient number of reversible electrodes actually give reversible thermogalvanic cells. The chief obstacle appears to be the high degree of reproducibility required of the electrodes. Such studies must, however, be left to others.

Comparing Galvanic and Thermogalvanic Cells

Published data on ordinary galvanic cells are far more plentiful than thermogalvanic data, and may be used to extend the latter to cases which have not been studied experimentally, using the principle that the thermodynamics of a given half-reaction is the same in reversible cells of either type. Intercomparisons require duplicating the half-reactions, and this means duplicating the electrodes, the solutions, and the external leads which conduct current through temperature differences. The same metal, copper, will be chosen for leads in all comparisons in order to systematize the results.

Consider a reversible galvanic cell and the two corresponding thermogalvanic cells with the same half-reactions:

$$M \rightarrow M^{++}(\text{in soln.}) + 2\ e^-(\text{in Cu})$$
$$H_2 \rightarrow 2\ H^+(\text{in soln.}) + 2\ e^-(\text{in Cu})$$

The overall reaction of the galvanic cell is then:

$$M + 2\ H^+(\text{in soln.}) \rightarrow M^{++}(\text{in soln.}) + H_2$$

Its potential will be denoted by the symbol $E_{M\text{-}H_2}$ and takes as positive if the reaction goes naturally in the direction indicated. If the cells are

reversible and the half-reactions have been duplicated, the thermodynamic relations between them may be written:

$$\left(\frac{dE}{dT}\right)_{M\text{-}H_2} = \left(\frac{dE^*}{dT}\right)_{M\text{-}H^{++}} - \left(\frac{dE^*}{dT}\right)_{H_2\text{-}H^+} \quad [5]$$

The cell or electrode reaction to which each term refers is identified by a subscript. The negative sign of the last term results from reversing the equation for the half reaction in the overall cell reaction.

Thermocouple Corrections

Consideration of a numerically unimportant but theoretically troublesome complication was postponed by using copper leads in all intercomparisons. The (dE*/dT) which is of direct interest in thermogalvanic corrosion is for leads composed of the individual electrode metal, and differs from that for copper leads by the dE/dT of a thermocouple composed of the two metals. The difference is small, usually negligible, hence the theory is kept straight and the calculations relatively simple by taking copper leads as standard and making the thermocouple correction to the basis of electrode metal leads when and if there is a special reason for the change.

The following discussion of the thermocouple correction is mostly for the purpose of fixing its sign. Using the data and notation of the International Critical Tables[4], the dE/dT of a thermocouple composed of metals M and R is denoted by $d(_ME_R)/dT$, and a positive sign indicates that positive current tends to flow from higher to lower temperature through M. Taking M as the electrode metal and R as copper, and assuming that $d(_ME_{Cu})/dT$ is positive, it follows that replacing the standard copper leads of a thermogalvanic cell by M, reduces the anodic tendency of the warmer electrode and hence also the dE*/dT of the cell. That is:

$$\left(\frac{dE}{dT}\right)^M = \left(\frac{dE}{dT}\right)^{Cu} - \frac{d(_ME_{Cu})}{T} \quad [6]$$

where the superscripts are used to identify the lead materials. The superscript Cu will be omitted hereafter, since copper leads are considered standard, and the use of any other metal will be indicated by a superscript. Values of $d(_ME_{Cu})/dT$ for most pure metals and many alloys can be found in the International Critical Tables, either directly or through an intermediate metal.

Calculation of the Standard dE*/dT of the Hydrogen Electrode

Direct comparisons of thermogalvanic coefficients, through equations such as Equation 5 are valuable in checking the validity of the assumptions and the reliability of data, but are of little use in predicting thermogalvanic coefficients, as not enough different kinds of electrodes can be used in any one solution, and the use of different solutions, connected through salt bridges, introduces uncertain liquid-junction potentials. For such purposes it is better to put the calculations on the basis of imaginary, hypothetical one molal solutions and use ordinary standard electrode potentials and other data which are on the same basis. In principle, the idea is to extrapolate data for actual solutions to infinite dilution, and calculate back to a

hypothetical concentration of one molal, following the laws of perfect solutions.

Comparisons will be made under standard conditions, indicated by the superscript °: 25°C, hypothetical 1 M solutions of the reactive ions, atmospheric pressure, and copper leads. All kinds of electrodes can be compared directly on this basis, as the difference between two standard (relative) potentials does not include a liquid-junction potential. If one standard $(dE^*/dT)^\circ$ is known, the others may be obtained from ordinary non-thermogalvanic data. The best available starting point appears to be Eastman's[5] correlation of dE^*/dT data for the calomel electrode with other data relating to the entropy of Cl^- (chloride ion). The data are for 15°C, 0.01 M solution of Cl^- in the presence of the equivalent concentration of a positive ion, and mercury leads. The half-reaction is:

$$Hg + Cl^- \text{ (in soln.)} \rightarrow HgCl + e^- \text{ (in Hg)}$$

The corresponding Gibbs-Helmholtz equation is:

$$\Delta S = S_{HgCl} + S_{e^- \text{ (in Hg)}} - S_{Hg} - S_{Cl^- \text{ (in soln.)}} = 23054\,(dE^*/dT)^{Hg} \quad [7]$$

The relative entropy of chloride ion, referred to that of electrons in mercury is:

$$S'_{Cl^-} = S_{Cl^- \text{ (in soln.)}} - S_{e^- \text{ (in Hg)}} \quad [8]$$

Eq. 7 then gives:

$$S'_{Cl^-} = S_{HgCl} - S_{Hg} - 23054(dE^*/dT)^{Hg} \quad [9]$$

Eastman collected and correlated the published data, and from them calculated a value of 28.0 e.u. (entropy units; cal./mol/°C) for a quantity which he called the absolute entropy of chloride ion and which differs from our S'_{Cl^-} only by a "transfer entropy" term which he introduced in an attempt to account for the effects of the other ions present on S'_{Cl^-}. Elimination of the transfer entropies from Eastman's figures gives the values of S'_{Cl^-} shown in Table I. The dE^*/dT values for HCl, LiCl, NaCl and KCl were measured directly; those for RbCl and NH_4Cl were calculated from related data.

The values of S'_{Cl^-} in the five neutral salt solutions are fairly consistent, and close to Eastman's value for the "absolute entropy," while that for HCl (hydrochloric acid) solution deviates considerably. The discrepancy for HCl is disturbing, but otherwise all indications point to the conclusion that the other solutions were sufficiently dilute to follow substantially the laws of perfect solutions on further dilution. Accordingly, the average value of S'_{Cl^-} from Table I as assumed to apply to *hypothetical* 0.01 M solutions of Cl^-.

Latimer, Pitzer and Smith[6] give an extensive table of standard relative entropies of aqueous ions in hypothetical one molal solution at 25°C, referred to that of H^+ as zero. The next problem is to convert the above value of S'_{Cl^-} to a standard basis of hypothetical one molal solution at 25°C and referred to conducting electrons in copper and thus to determine the difference between the two standard relative scales.

The correction to hypothetical 1 M solution is made by means of the ideal "volume-ratio" rule, according to which the increase in entropy resulting from dilution from M_1 to M_2 is equal to $R \log_e M_1/M_2$,

where R is the gas constant and equals 2 cal./mol/°C. The correction therefore amounts to 2 x 2.3 = 4.6 e.u. for each tenfold dilution, or 9.2 e.u. for a hundredfold dilution. It is roughly estimated that the corrections from 15°C to 25°C, and from mercury to copper leads together amount to 0.3 e.u. The final result for the relative entropy of chloride ion at 25°C in hypothetical 1 M solution referred to that of conducting electrons in copper as zero, is then:

$$S'_{Cl^-}{}^{\circ} = 27.7 - 9.2 + 0.3 = 18.8 \text{ e.u.} \quad [10]$$

Latimer, Pitzer and Smith's value for the standard relative entropy of chloride ion under the same conditions but referred to that of H^+ as zero, is 13.5 e.u. The difference between the two values, 13.5 — 18.8 = -5.3 e.u., is the calculated differences between the two relative scales (for univalent ions), and means that, according to these calculations, the standard relative entropy of H^+, referred to that of conducting electrons in copper as zero is:

$$S'_{H^+}{}^{\circ} = S_{H^+} \text{ in soln.} + S_{e^-} \text{ in Cu} = -5.3 \text{ e.u.} \quad [11]$$

The standard thermogalvanic coefficient of the hydrogen electrode may now be obtained as follows:

$$\tfrac{1}{2} H_2 \rightarrow H^+ \text{ (in soln.)} + e^- \text{ (in Cu)}$$
$$\Delta S = S_{H^+} \text{ in soln.} + S_{e^-} \text{ in Cu} - \tfrac{1}{2} S_{H_2}$$

The Gibbs-Helmholtz equation then gives, for standard conditions:

$$23054 \left(\frac{dE^*}{dT}\right)^{\circ}_{H_2 - H^+} = S'_{H^+}{}^{\circ} - \tfrac{1}{2} S^{\circ}_{H_2} \quad [12]$$

Substituting the value of $S'_{H^+}{}^{\circ}$ from Equation 11, and Giauque's[7] value of 15.61 e.u. for $\frac{1}{2}S^{\circ}_{H_2}$:

$$\left(\frac{dE^*}{dT}\right)^{\circ}_{H_2 - H} = \frac{-5.3 - 15.61}{23054} = -0.00091 \text{ volts/°C.} \quad [13]$$

Equation 13 gives the desired result. While further data would be required for a reliable estimate of its accuracy, it is believed that the error in $S'_{H^+}{}^{\circ}$, which determines that in the final result, is less than 3 e.u., corresponding to an error of about 0.00013 volts/°C or 14 percent. This accuracy is sufficient for present purposes, but no doubt could be greatly improved through a systematic investigation of ionic entropies.

Calculation of (dE*/dT)° for Other Electrodes

The (dE*/dT)° values of other electrodes can be obtained by comparing each in turn with the standard hydrogen electrode. Equation 5 takes the form:

$$\left(\frac{dE^*}{dT}\right)^{\circ}_{M - M^{++}} = \left(\frac{dE}{dT}\right)^{\circ}_{M - H_2} - 0.00091 \text{ (volts/°C)} \quad [14]$$

where -0.00091 is the value of $\left(\frac{dE^*}{dT}\right)^{\circ}_{H_2 - H}$ from Eq. 13. With appropriate changes in subscripts, Equation 14 applies to any reversible electrode.

Values of $\left(\frac{dE}{dT}\right)^{\circ}_{M - H_2}$ are not generally available as such, but in many cases they can be calculated from readily available data through the alternate form of the Gibbs-Helmholtz equation shown in Equation

1, which for standard conditions becomes:

$$\left(\frac{dE}{dT}\right)^{\circ}_{M-H_2} = \left[\frac{\Delta H^{\circ}}{23054\ n} + E^{\circ}\right]\frac{1}{298} \qquad [15]$$

ΔH° is the heat evolved when one mol of metal is oxidized and the equivalent amount of hydrogen displaced from solution as the $M-H_2$ reaction occurs irreversibly in dilute solution. It may be calculated from Bichowsky and Rossini's[8] values of Q_f (heat evolved on formation from the elements) of the ions which enter into the half-reaction at the M electrode, which are on the relative basis referred to that of H^+ as zero, and for dilute solutions. Division by 23054 n reduces ΔH° from cal./mol to volts. E° is the standard (relative) potential of the M electrode, referred to that of the hydrogen electrode as zero, and is taken as positive if the metal displaces hydrogen from solution. Values of E° for a large number of electrodes are given in Latimer and Hildebrand's[9] table of standard oxidation-reduction potentials; values from other sources should be checked for sign. The factor 298 is the absolute temperature corresponding to 25°C. The working equation, obtained by combining Equations 14 and 15, is:

$$\left(\frac{dE^*}{dT}\right)^{\circ} = \left[\frac{\Delta H^{\circ}}{23054\ n} + E^{\circ}\right]\frac{1}{298} - 0.00091 \qquad [16]$$

Subscripts are omitted in Equation 16, as $(dE^*/dT)^{\circ}$, ΔH° and E° all refer to whatever electrode reaction is being compared with that of the hydrogen electrode.

Table III shows the values of $(deE^*/dT)^{\circ}$ of a number of electrodes as calculated from Equation 16 using data from the sources[8, 9] mentioned above. The following examples illustrate the calculations.

The Cu-Cu^{++} Electrode

The half-reaction is:

$$Cu \rightarrow Cu^{++} + 2\,e^- \text{ (in Cu)}$$

Q_f for Cu^{++} is given as -15.1 kcal, which means that 15100 cal. are absorbed when one mol of copper irreversibly displaces one mol of H_2 from solution; and $n=2$. Hence $\Delta H^{\circ}/23054\ n = 15100/46108 = 0.328$ volts. E° for this electrode is given as -0.344 volts. Then by Equation 16:

$$\left(\frac{dE^*}{dT}\right)^{\circ}_{Cu\text{-}Cu^{++}} = \left[0.328 - 0.344\right]\frac{1}{298} - 0.00091$$

$$= -0.00096 \text{ volts/°C} = -0.96 \text{ mv/°C}$$

It may be noted that the "Thomsen Rule" predicts a value of zero for the bracketed term of Equation 16 which would make $(dE^*/dT)^{\circ}$ the same for all electrodes. This rule is unreliable, but comes fairly close to the truth in many cases. The thermocouple correction is zero in this case, as the electrode metal is copper.

The Pt-Cl^- - $PtCl^-_4$ Electrode

The half-reaction is:

$$Pt + 4\,Cl^- \rightarrow Pt\,Cl^-_4 + 2\,e^- \text{ (in Cu)}$$

Q_f for $Pt\,Cl^-_4$ is given as 122.2 kcal. and Q_f for Cl^- as 39.687 kcal.; and $n=2$. E is given as -0.73 in the latest

table, correcting the earlier value of "about" -0.2. Accordingly:

$$\frac{\Delta H^\circ}{23054\ n} = \frac{4 \times 39687 - 122200}{46108} = 0.791 \text{ volts.}$$

$$\left(\frac{dE^*}{dT}\right)^\circ_{Pt - Cl^- - PtCl_4^-} = \left[0.79 - 0.73\right]\frac{1}{298} - 0.00091$$

$$= -0.00071 \text{ volts/°C} = -0.71 \text{ mv/°C}$$

The thermocouple correction to platinum leads is of the order of 0.003 mv/°C, and negligible in comparison with the error in Equation 10.

Discussion of Table III. Some of the $(dE^*/dT)^\circ$ values in Table III have only theoretical interest. Table III was made up without regard for actual reversibility and includes some irreversible electrodes such as $Al\text{-}Al^{+++}$ and $Hg\text{-}Hg^{++}$ which cannot possibly enter into thermogalvanic action, and others for which thermogalvanic action is possible only under special conditions if at all. How to determine whether thermogalvanic action can occur in a given case is discussed in the next section.

In using Table III to predict corrosion potentials, thermocouple corrections should theoretically be made to convert $(dE^*/dT)^\circ$ to the basis of electrode-metal leads. Most of the corrections are considerably less than 0.01 mv/°C; the largest ones are about 0.02 mv/°C for iron leads and -0.02 for nickel leads. Considering the uncertainties in the tabular values themselves, the thermocouple correction is negligible in all cases listed. But the thermocouple correction may sometimes be significant, for instance in work designed to improve the accuracy of Equation 14.

In applying Table III to actual solutions, the best than can be done, in the absence of further data, is to ignore the difference between hypothetical and actual concentrations and assume that the entropies of the reactive ions change with dilution in accordance with the volume-ratio rule. For example, in the simple case where only the metal ion is involved, each ten-fold dilution algebraically increases the entropy of the ion and the Peltier entropy change by 4.6/n e.u., and dE*/dT by 4.6/23054 n volts/°C. Thus for the typical case of a divalent metal and a negative dE*/dT, each ten-fold dilution theoretically reduces dE*/dT by 0.10 mv/°C. Thus it takes a rather large change in concentration of reactive ion to produce important changes in dE*/dT. This fact in a measure justifies neglecting the differences between hypothetical and actual concentrations, in simple cases. However, it is not permissible to ignore complex formation between the metal ion and an ion present in the solution; the half-reactions are essentially different in such cases and should be studied individually. The $Pt - Cl^- - PtCl_4^-$ half-reaction is the only one of this sort listed in Table III, but many others arise in practice, such as $Cu - Br^- - CuBr_3^-$.

The errors involved in applying Table III to reversible thermogalvanic cells fall into three classes. The error in $(dE^*/dT)^\circ_{H_2 - H^+}$ produces a systematic error which affects the whole table. Errors in the individual values of $(dE/dT)^\circ$ for metal-hydrogen cells produce corresponding errors in the individual $(dE^*/dT)^\circ$'s; and deviations from the volume-ratio rule produce errors in the cor-

TABLE III

Standard thermogalvanic coefficients for various electrodes, from heats of formation and standard potentials, for hypothetical one molal solutions at 25° C. and copper leads, on the basis that (dE*/dT)° of the standard hydrogen electrode is —0.91 mv/°C. Positive values mean that the metal tends to plate from the warmer to the colder electrode.

Electrode	(dE*/dT)° mv/°C	Electrode	(dE*/dT)° mv/°C
$Mg\text{-}Mg^{++}$	—1.11	$Cd\text{-}Cd^{++}$	—0.84
$Al\text{-}Al^{+++}$	—1.45	$Sn\text{-}Sn^{++}$	—0.61
$Fe\text{-}Fe^{++}$	—0.93	$Pt\text{-}Cl^{-}\text{-}PtCl_4^{--}$	—0.71
$Ni\text{-}Ni^{++}$	—1.18	$Hh\text{-}Hg_2^{++}$	—0.68
$Cu\text{-}Cu^{++}$	—0.96	$Hg\text{-}Hg^{++}$	—0.75
$Zn\text{-}Zn^{++}$	—0.99	$Pb\text{-}Pb^{++}$	—0.50
$Ag\text{-}Ag^{+}$	+0.07		

rections for concentration in individual applications.

Only sketchy experimental checks are available. Berry's[1] data on an acid sulfate Cu-Cu^{++} cell with 0.94 M Cu^{++} gave an average dE*/dT of -0.965 mv/°C between 16.5 and 100°C, which happens to be in practically perfect agreement with the calculated (dE/dT)°, neglecting the effects of temperature and of differences between hypothetical and actual concentrations. The data at lower Cu^{++} concentrations show changes in the direction but only very roughly of the magnitude predicted by the volume-ratio rule. It has also been observed that the positive dE*/dT of the $Cu\text{-}Br^{-}\text{-}CuBr_3^{-}$ cell increases with decreasing concentration of cuprous copper at constant bromide concentration, as it should; but again the changes do not agree quantitatively with the predictions of the volume-ratio rule.

It is believed that most of the values of Table III are correct within 0.2 or 0.3 mv/°C. Additional errors in applications to particular solutions, due to deviations from the volume ratio rule, undoubtedly depend very greatly on the particular solution, being small in dilute solutions and larger in more concentrated solutions, especially in cases which involve complex formation. The deviations can readily be measured in well-behaved cells and are well worth investigation.

Cells which are involved in thermogalvanic corrosion are necessarily sufficiently reversible to make measurements possible. Since actual measurements are possible in the practically important cases, the chief value of Table III is for general qualitative purposes for which the errors do not matter much. It is safe to conclude that thermogalvanic potentials are generally of the order of several tenths of a millivolt per degree Centigrade and vary with the electrodes and the solution. The potentials of simple metal-metal ion cells are in most cases negative, that is, metal tends to plate from the colder to the warmer surface; but this is not a general rule. Positive potentials are also found, especially in cases where the half-reaction is complicated by the formation of complex ions.

Rate Factors

The overall driving force for thermogalvanic corrosion is the reversible potential E*, which equals the product of the temperature difference between the hot and cold metal surfaces and the average dE*/dT. E* is apparently not likely to exceed ± 0.1 volt. It seems unnecessary to dwell upon the importance of temperature differences, and dE*/dT has already been discussed at length.

The anodic current density is what really matters in corrosion, and

E* is only one of many factors which determines it. All cells, including those which behave reversibly during open-circuit potential measurements, develop irreversibility as current is allowed to flow. Electrolytic resistance and concentration polarization produce back emf in the solution, but the electrical resistance of the metal is seldom large enough to have appreciable effect. Protective films, passivation and energy barriers cause electrical resistance or overvoltage effects at one, or more likely both electrodes. A corrosion cell is a short-circuited cell; the current settles down at a value such that the sum of the black emf's from all sources equals the reversible E*. The lower the anodic current density at which this occurs, the better the protection against thermogalvanic corrosion. A given degree of irreversibility generally gives better protection against thermogalvanic corrosion than it does against other forms of electrolytic corrosion, because of the relatively small magnitude of thermogalvanic potentials. Serious thermogalvanic corrosion is possible only through highly reversible electrode reactions. The factors which determine thermogalvanic corrosion rates are familiar ones, although there are some new angles to be considered.

Protection of Iron

For example, if iron is anodically protected against ordinary electrolytic corrosion accompanied by hydrogen formation, it is also protected against thermogalvanic corrosion. Cathodic overvoltage for deposition of metal protects against thermogalvanic corrosion, but cathodic overvoltage for deposition of hydrogen does not. It is to be remembered that in thermogalvanic corrosion, the metal dissolved from the anode is deposited on the cathode; this discussion is not concerned with the effects of temperature or temperature differences on other forms of electrolytic corrosion, for which the driving force is not the thermogalvanic potential.

One outstanding peculiarity of thermogalvanic corrosion is the regeneration at the anode of the oxidizing agent which is used up at the cathode, which makes thermogalvanic corrosion self-perpetuating and indefinitely increases the amount of damage which can be done by a given amount of oxidizing agent. As Berry[1] emphasized, this means that thermogalvanic corrosion can begin only if oxidizing agent is already present at the cathode, and in the long run can proceed only as fast as regenerated oxidizing agent reaches the cathode. Limiting the amount of oxidizing agent, and the rate at which is can reach the cathode, are therefore important means of controlling thermogalvanic corrosion.

The oxidizing agent is the oxidized form of the metal corroded and for reasons which will be made apparent, is practically always in solution, as a "reactive ion." The reactive ion is transported by the corrosion current, but never as fast as it is used or produced; and if a negative complex ion is formed, it travels in the wrong direction. If no other means of transport of the reactive ion from anode to cathode were available, the corrosion current would quickly choke itself off through concentration polarization.

Diffusion is slow, and effective over short distances only; most cases of severe thermogalvanic corrosion depend primarily on motion of the solution to transport the reactive ion.

Factors in Corrosion Rate

High concentration of reactive ion, circulation of solution between hot and cold zones, and stirring of the solution adjacent to the electrode, all tend to facilitate transport of the reactive ion, reduce concentration polarization, and speed up corrosion. High electrical conductivity of the solution favors rapid corrosion, and low conductivity, as in nearly pure water, inhibits corrosion. As Berry's data show, appreciable thermogalvanic currents may be obtained even though the concentration of the active ion is quite low, if conductivity of the solution is high and circulation rapid, and electrode reactions are highly reversible.

The concentration of reactive ion depends on conditions in the individual case. The reactive ion may be an essential constituent of the solution, or an unwanted impurity. It may come from solution of oxide films or scale on the metal, or from any of numerous other oxidizing sources. Processes which are not parts of the thermogalvanic cycle may produce or destroy reactive ion, and there may be a balance between such processes. The solubility of the corrosion product sets an upper limit for the concentration of the reactive ion.

Limiting Factor

The low solubility of many corrosion products is a very important factor limiting the practical importance of thermogalvanic corrosion. Theoretically, an excess of a nearly insoluble corrosion product, well distributed over sufficient cathodic area, might substitute for the reactive ion as the corrosive agent, but practically, half-reactions involving nearly insoluble non-conductive compounds are slowed down by concentration polarization, and even if they are reversible under open-circuit conditions, which is by no means always the case, the anodic current density is low. Furthermore, such a process would usually be choked off eventually, through failure of part of the regenerated oxidizing agent to reach prospectively cathodic surfaces.

Severe thermogalvanic corrosion is probably possible in some cases where the solubility is low but still appreciable, say in the range of 0.0001 - 0.001 M, and other conditions favor it. With solubilities a few orders of magnitude lower, as for so-called insoluble corrosion products, thermogalvanic corrosion becomes exceedingly improbable. The solubility of a corrosion product, of course, depends very largely on the solution; in many cases, on the pH. For example, no thermogalvanic current could be detected between oxidized copper electrodes in slightly alkaline sodium sulfate solution. But Cu^{++} can be formed by adding an acid, or a complex cuprous chloride ion by adding a chloride, and either will sustain a thermogalvanic current.

Rapid Penetration

Short distances between hot and cold surfaces of metal favor corrosion; and small anode area and large cathode area favor rapid penetration

of the metal. Thus corrosion tends to be concentrated at sharply localized hot spots when dE*/dT is positive, and at sharply localized cold spots when dE*/dT is negative. Either condition can arise in heat exchange equipment. Even small temperature differences may produce rapid penetration if the temperature gradient in the metal is steep enough.

Ability to Plate

The practical question of whether or not thermogalvanic corrosion is possible in a given system can often be answered from a knowledge of whether ordinary constant-temperature electroplating is possible, with the same metal and solution, and an external potential which is limited to the thermogalvanic range of say 0.1 volt or less. Of course, the solution must contain an initial supply of the expected anodic oxidation product (reactive ion), in such concentrations as would be expected in practice from sources other than thermogalvanic corrosion.

Failure of an applied potential of 0.1 volt to produce a substantial anodic current density, or to plate metal from the anode to the cathode, implies that thermogalvanic corrosion is impossible under the test conditions. For example, aluminum cannot be plated out of water solutions, and therefore, is immune to thermogalvanic corrosion; and overvoltage effects make chromium so difficult to plate that it is practically sure to be immune.

Iron, nickel, zinc, cadmium, and tin can all be plated from one electrode to another, and so may be suspected of being subject to thermogalvanic corrosion under some circumstances. However, it is evident that rather special conditions would be required. There is substantially no danger with solutions in which the oxidation product is not appreciably soluble; and conditions which make the oxidation product soluble also tend to produce ordinary corrosion by way of hydrogen formation, and thus to make it unimportant whether further corrosion occurs by the thermogalvanic route or not.

Several attempts to produce thermogalvanic currents between iron electrodes have been made in this laboratory, but all have failed. Apparently the overvoltages of iron in contact with most solutions are high enough to provide adequate protection. The same is doubtless true of nickel, and probably of zinc, cadmium and tin as well. Nevertheless, it is suspected that conditions may exist for any of these metals which would make thermogalvanic corrosion possible.

Copper, silver and lead are known to be subject to thermogalvanic corrosion under some circumstances. This would be expected, as all can readily be plated through a variety of solutions. Whether still more noble metals such as gold and platinum may be also as suggested by Berry,[1] is purely a question of the overvoltages in particular cases.

Solutions which cause thermogalvanic corrosion are likely to be ones which, from an electroplater's point of view, have poor "throwing power": because good throwing power, or ability to plate relatively evenly in spite of projections and recesses, requires relatively high cathodic overvoltage. The formation

of "trees" instead of a smooth surface plate, shows conspicuously poor throwing power, and indicates that the cathodic overvoltage is low and suggests the probability of thermogalvanic corrosion.

Further Discussion

No review of the literature is attempted, but a few references to prior work on thermogalvanic corrosion are discussed briefly. Wesley, Trebler and LaQue[10] recognized the possibility of thermogalvanic corrosion and attempted to calculate the standard dE*/dT of nickel through the use of the Gibbs-Helmholtz equation. Their general ideas were correct up to a certain point, but they failed to take account of the fact that the standard emf and heat of formation data which they used were on the relative instead of the absolute basis, and so omitted the dE*/dT of the hydrogen electrode in their calculation.

In the discussion following a paper by W. Z. Friend, A. H. Maude[11] called attention to the fact that a copper steam coil goes to pieces in a few minutes when used to boil hydrochloric acid solution, although test specimens at the same temperature last for days, and ascribed the failure to what is here called thermogalvanic corrosion. Maude's explanation is undoubtedly correct. The reactive ion would be a copper chloride complex formed by oxidation of the copper, presumably by dissolved air. The dE*/dT would be positive, and copper would plate from hotter to colder areas, just as Maude reports.

In a paper on the causes of corrosion currents, Mears and Brown[12] reported the potentials produced by differential heating of pairs of electrodes 2 S - ½ H aluminum (commercially pure, half-hard), 18 - 8 stainless steel (18 percent Cr, 8 percent Ni), and copper, in 10 percent sodium chloride solution, and ascribed them to differences in solution pressure of the metal, produced by differential heating. Although this apparently indicates that they assumed a thermogalvanic mechanism in each case, inclusion of aluminum makes it obvious that they did not mean to imply that the metals were plated from one surface to another. Plating could not have occurred in the case of aluminum, and presumably did not in the case of stainless steel. In these two cases, the cathode reaction might have been liberation of hydrogen, or reduction of atmospheric oxygen, among other possibilities. Undoubtedly the anode reaction was the oxidation of metal in all three cases. It is safe to say that the cell reaction was truly thermogalvanic in the case of copper, perhaps somewhat modified by concentration-cell effects.

In tests similar to theirs, we found that various combinations of differential aeration and differential heating of copper electrodes in either 0.1 molar sodium sulfate or 0.2 molar sodium chloride produced potentials of as much as 0.1 volt. The directions and magnitudes of the potentials varied rapidly, as oxidation of the electrodes produced changes in the amounts and distribution of copper in the solution. It was even possible to make an aerated electrode behave as anode. The results clearly indicated that the

electrodes never behaved as oxygen electrodes or as copper-copper oxide electrodes, but only as $Cu-Cu^{++}$ electrodes in sodium sulfate solution and as copper-complex cuprous chloride ion electrodes in sodium chloride solution; and that the potentials were of thermogalvanic and concentration cell origin, and depended on the preliminary oxidation of copper to provide the reactive ion.

Acknowledgment

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Discussion

*By J. T. Waber**

In work now being prepared for press,** it has been shown that the silver ion is associated with two water molecules. It seems that this fact is in accord with Mr. Buffington's data, which indicate that silver forms some complex in aqueous media.

* Ill. Inst. of Technology, Chicago, Ill.
** Podolsky and Longtin; "Nature of Aqueous Silver Ions."

Discussion of Paper, Location and Selection of Anode Systems for Cathodic Protection*

By R. A. Brannon*

MR. GOOD presents information in his article which will be useful to those corrosion engineers who must deal with the complex problems encountered in the selection of proper locations for anodes and of the design of proper types of anode systems.The reader may gain the impression from the beginning of this paper that here is another set of calculations based upon assumed conditions that one seldom, if ever, actually encounters. The uniform soil resistivity, for instance, which is assumed for the calculation of resistance of anode systems having various configurations, various lengths, and various depths of burial would rarely occur in actual soils, and once found could not be expected to prevail throughout the various seasons of the year.

The information given in Table I shows, however, that the calculated and the actual total circuit resistance agree remarkably well. The differences between actual and calculated values of from 0.0 to 14.2 percent indicate that the methods may be used with confidence. The author would doubtless want to take the precaution of adding that allowance would need to be made for local conditions.

Any discussion of anode configuration must necessarily be limited to a few of the innumerable possible configurations. It would be interesting, however, to know the effect of breaking the 360 feet of 6-inch pipe buried horizontally, which was used for most of the illustrations, into two or more sections and placing them varying distances apart. Actual cases have been observed where distributing horizontal anodes over a considerable area have resulted in unusually low total circuit resistances. It is assumed that the curves in Figure VI showing "Resistance in Percent vs Spacing Between Rods in Rod Diameters" refer to vertical rods and could not be applied to horizontal rods or sections of pipe.

This good paper could be made more complete by the inclusions of a description of the method used in determining the pipe-line resistance to earth (R_{p1}) or a reference to the literature concerning it.

★ Good, D. B., Corrosion 3, 11. (Nov.) 1947.

* R. A. Brannon, Humble Pipe Line Company, Houston, Texas.

Further Discussion of Paper, Location and Selection of Anode Systems for Cathodic Protection★

By O. C. Mudd*

CALCULATIONS for individual anode resistances or the resistance of a composite group of anodes, termed "a ground-bed," are practical where soil resistivity changes are relatively gradual, both in respect to horizontal distance and depth; also where the symmetry of the ground-bed pattern can be maintained.

Conditions are encountered where soil resistivity changes are abrupt with respect to horizontal and vertical. These conditions result in the adoption of devious ground-bed patterns, irregular spacing and depth of anodes to permit anode placement in lowest resistivity soil. Deviation of pattern complicates calculations; variations in depth adds to this and abrupt soil resistivity changes introduce qualifying factors beyond practical use.

Such erratic conditions are most frequently encountered where soil formations are composed of successive thin stratum and these condi-

★ Good, D. B., Corrosion 3, 11, (Nov.) 1947.

* Chief Corrosion Engineer, Shell Pipe Line Corp., Houston, Texas.

TABLE I

INSTALLATION			INDIVIDUAL ANODES—RESISTANCE					
No.	No. of Anodes	Bed Res.	No. 1 Res.	No. 2 Res.	No. 3 Res.	No. 4 Res.	No. 5 Res.	No. 6 Res.
1	4	.757	2.25	3.91	2.37	3.50	....	....
2	6	.342	1.71	1.80	1.63	1.64	2.03	1.72
3	6	.330	1.01	2.73	2.32	2.47	2.36	1.30
4	6	.475	2.04	3.37	2.15	2.53	2.70	2.28
5	6	.326	1.58	1.50	1.55	1.51	1.76	1.50
6	6	.521	3.90	2.66	3.19	3.36	2.24	2.60
7	6	.248	1.70	1.13	1.42	1.49	1.16	.96
8	6	.303	1.83	1.85	1.64	1.69	1.54	.89
9	6	.268	1.38	1.59	1.48	2.11	.82	1.49
10	5	.264	.94	1.18	1.47	.90	1.13	....
11	6	.390	1.87	1.67	2.13	1.60	1.53	1.79

TABLE II

	ANODE		SOIL RESISTIVITY FOUR ELECTRODES SPACED—			
Inst. No.	No.	Res.	5′	10′	20′	30′
4	4	1.97	1017	842	1494	1955
4	5	2.39	1122	842	1494	1955
8	6	.89	824	575	652	689
9	6	1.49	718	555	575	575
1	1	2.25	1055	683	842	1210

tions may be further complicated by previous erosion, followed by succeeding sedimentary deposits.

Soil resistivity variations encountered during investigations for eleven ground-bed locations (totalling 66 anodes) are illustrated in the accompanying family of curves prepared from measurements made at the 66 locations by the four electrode method.

The respective anode resistances to soil after installation are given in Table I.

Variations of some individual anode-to-soil resistances were due to the interference effect of adjacent anodes, others varied because of soil resistivity changes in the horizontal plane.

Anodes were large iron castings weighing around 2000 pounds each, such as engine beds, fly wheels or similar masses. The average effective dimension for resistance calculations of such anodes had been found as near equivalent to a three-foot diameter sphere. The spacings between anodes were maintained at 50 diameters (150 feet) when possible and the average depth of burial was eight feet.

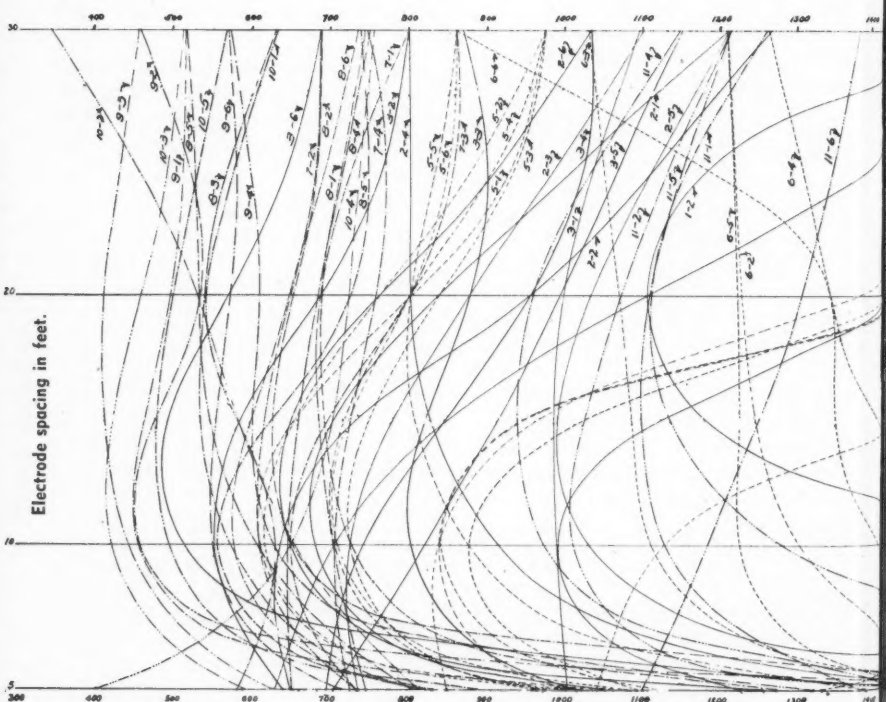

Table II shows variations in anode-to-soil resistances where vertical soil resistivity changes are nearly equivalent.

Anodes 4-4 and 4-5 were located in the ground-bed pattern where interference from adjacent anodes was nearly identical.

Anodes 8-6 and 9-6 were located with respect to other anodes which should have caused the resistance of 8-6 to be the greater.

Anode 1-1 was located in a pattern where minimum interference should occur, however, it is to be noted that the anode-to-soil resistance is greater than 4-4, which was subject to more interference. Soil resistivity measurements for 1-1 indicated a potential lower anode resistance.

The above illustrates irregularities that may be encountered and are intended as a note of caution to those who have never experienced these unusual conditions, and attention is called to the limitations of calculations when qualifying factors of a formula cannot be determined or may be impractical.

In such cases it is better to design for the least to be expected.

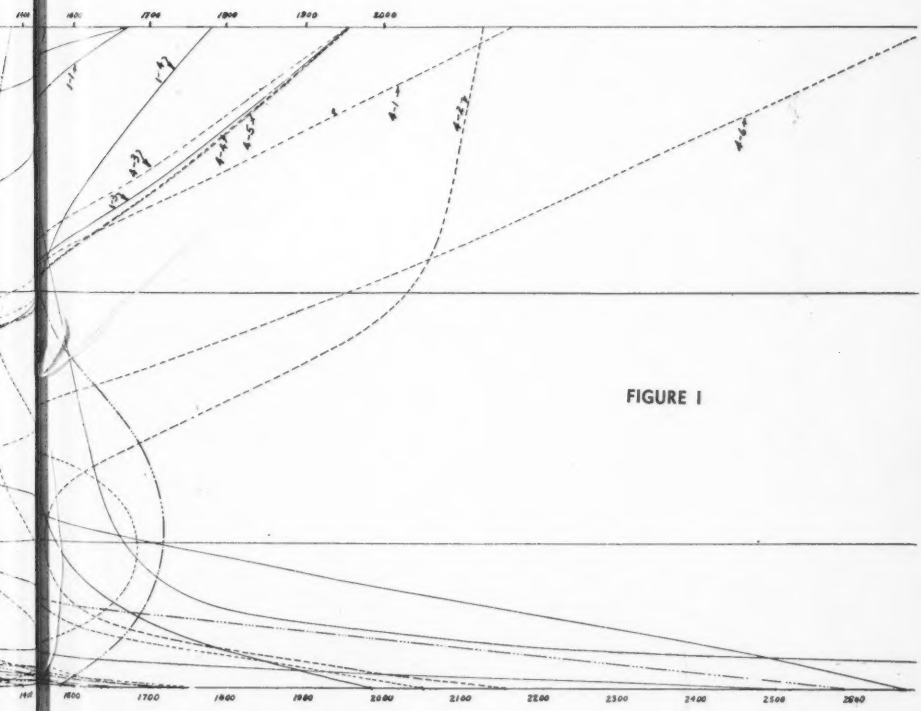

FIGURE 1

NACE News

REGIONAL, LOCAL SECTION ACTIVITIES

Members of the National Association of Corrosion Engineers were extremely active in recent weeks, during which time four Regional Divisions and four Local Sections held meetings. New officers were voted upon and elected in the Western, North East, South East and South Central Regions. Reports from various areas follow.

South Central Region

Coupling business and pleasure—but keeping each in its definite place and time, success crowned the efforts of officials of the South Central Regional Division in staging their first Annual Meeting. Approximately 150 members and their guests attended the two-day meeting, which was held October 26 and 27 in Houston, Texas. Eleven technical papers were presented, and much lively discussion followed presentation of each. A business meeting climaxed the session, during which new officers were elected, and voted into office effective immediately, October 27.

The first day of the session was highlighted by a technical session at the Texas State Hotel in the afternoon, and in the evening by an excellent dinner, which was coupled with excellent entertainment and refreshments through courtesy of manufacturers and distributors. More than 100 persons attended the dinner, which was held at Ye Olde College Inn.

Nathan Schofer, Cities Service Refineries, Lake Charles, La., was chairman of the inaugural day's session, at which, in the absence of A. N. Horne, chairman of the Region, L. F. Scherer, chief engineer for the Texas Pipe Line Co., Houston, and NACE Regional Director, welcomed the large crowd. Mr. Schofer then introduced B. J. Kalb, Precision Instrument Co., Houston, who started the technical proceedings by reading the paper, Radium for Determining Corrosion Progress in Production and Refinery Equipment. The author explained how the presence and extent of inside pipe and small tank corrosion could be determined through the use of photographs made by using reflected energy from radium. Radiation from radium, after passing through the piece to be tested strikes a sensitized film; the density of the exposed film varies inversely with the thickness of the metal. Photo-electric cells are then used to measure the density of the exposed film to determine the amount of metal lost. One advantage of this method of radiographic inspection of metals is its reproducibility. The equipment is portable, being compact and light in weight,

making it easily available for use on almost any equipment. An aside from the technical points brought out by Mr. Kalb was that 300 millograms of radium, with a value of approximately $30,000, are used in connection with the test equipment. Once set up in the field, the radium is left on location, and without guard, until the test run is completed. Since it is highly active, locating the radium in the field presents no problem. It was also pointed out that the radium is safe to handle, and the fact that it was radium kept "Sidewalk Superintendents" at a safe distance.

S. S. McGill, chief engineer of the International Paper Co., Springhill, La., then told of the many and varied problems involved in handling some of the extremely corrosive mixtures encountered in the paper industry. Monel and stainless steel are used to considerable extent, and concrete linings have been found to give excellent results in some cases.

Harry Shephard, National Carbon Co., Houston, concluded the first day's technical session with the audience-interest holding paper, Non-Metallic Materials for Corrosion Resistance in Chemical Plants and Refineries. The author described the advantages of using carbon and graphite when handling corrosive materials. Both carbon and graphite are highly resistant to corrosion in all except strongly oxidizing media, and both have a low coefficient of thermal heat transfer, thus are resistant to thermal shock. Carbon is cheaper, has a low heat transfer coefficient, but is fairly difficult to machine. On the other hand, graphite is more expensive than carbon, has a higher heat transfer coefficient and is easier to machine.

Monday's sessions were held in the Auditorium of the United Gas Bldg., and the morning meeting was presided over by C. W. Evans, of United Gas Pipe Line Co., Shreveport, La. The first speaker introduced was Lyle R. Sheppard, Shell Pipe Line Corp., Houston, who told of his work on sulfide corrosion as encountered internally in pipelines. He has found that free sulfur is formed in distribution lines by reaction of ferric chloride and hydrogen sulfide. The free sulfur formed is a great deal more corrosive than hydrogen sulfide, and reacts with the steel pipe wall to form magnetic iron sulfide, which is also corrosive. Mr. Sheppard warned of the danger of adding inhibitors without making a thorough study of the system. The compound that acts as an inhibitor at one point, may actually increase corrosion at another, if conditions change.

Two related papers, Utilization of Electrically Insulated Couplings in Corrosion Control, and Mechanical Design Features in Insulated Couplings, were presented by W. F. Levert and Lee Spinks, respectively, and both of United Gas. Mr. Spinks substituted for Paul Williams. These

Coming NACE Meetings

CORPUS CHRISTI (Texas) Section, South Central Region, meets the third Wednesday evening of each month.

SHREVEPORT (Louisiana) Section, South Central Region, meets the second Thursday evening of each month.

NACE ANNUAL CONFERENCE and Exhibition, Hotel Jefferson, St. Louis, Mo., April 5-8, 1948.

papers showed how sections of a line can be blocked off by the use of insulating couplings so that proper protection can be given. An example of this is the insulation of lines at the wellhead from the coring and tubing of the well itself, preventing currents on the line discharging into the well metal. Slides were used to show placement of insulating gaskets and washers as used in the couplings.

The session was recessed for lunch following a color film taken by Wm. E. Huddleston, consultant, Bartlesville, Okla., showing the installation of magnesium anodes. A jeep equipped with power auger, ditching attachments and dozer blade were used to simplify anode installation.

The afternoon term, presided over by W. H. Stewart, Sun Pipe Line Co., Houston, got under way with a "Report on Polycote" by Forbes Cross, Kansas City Testing Laboratory, Kansas City, Mo. According to Mr. Cross, this newly developed coating has excellent mechanical properties regarding strength and flexibility. An unexplained phenomena encountered during tests was that the material increased in electrical resistance while in contact with a 10 percent salt solution.

Derk Holysteyn, Shell Oil Company, Houston, then gave a slide discussion of cathodic protection as used in the orientation of company employees. The action of cathodic protection was explained by placing common nails in an agar gel containing potassium ferricyanide and phenolphthalien. Anodic areas were shown by a blue color, cathodic areas by a red color.

B. G. Cole, chief chemist, Water Department, City of Shreveport, La., told of corrosion problems peculiar to water systems. Corrosion is particularly severe in conditions where the heater is operated above capacity, or where the water temperature is maintained too high. Corrosion products sometimes build up inside mains so that pressure and capacity are only a fraction of the original pipe.

J. A. Holloway, Houston Pipe Line Co., gave a demonstration on the use of thermite for bonding Dresser couplings, after which Mr. Scherer called the business meeting to order.

New Officers

The new officers are as follows: Don B. Good, Texas Pipe Line Co., Tulsa, Okla., chairman; Nathan Schofer, Cities Service Refinery, Lake Charles, La., vice chairman.

In view of the difficulties attached in having a new officer take over the secretary-treasurer's duties, a precedent was established by electing an assistant secretary-treasurer, who will assist the present secretary until the expiration of the term, then automatically take over full charge, with another assistant being elected at that time. Thus T. F. P. Kelly, James E. Mavor Co., Houston, was

Notice

• Effective January 1, 1948, subscription to the National Association of Corrosion Engineers' journal, CORROSION, will be $7.50 per year, with a $3.50 per year rate extended to educational and public libraries. The present method of allocating $3.00 of Members' $7.50 dues for a subscription to CORROSION will continue in force.

reelected secretary-treasurer, and T. R. Stathem, Magnolia Pipe Line Co., Dallas, Texas, was named as assistant secretary-treasurer.

New Committee Formed

A. W. McAnneny, Texas Pipe Line Co., Houston, was elected chairman of a Regional Committee, to be known as the Committee on Internal Tank Corrosion, for purpose of cooperating with an unattached corrosion group now studying the problem in the West Texas and New Mexico areas.

Besides Regional and Local officers, those present included the following officers of the parent Association: President G. R. Olson, Treasurer O. C. Mudd, Executive Secretary A. B. Campbell, and Director Tom L. Holcombe.

Messrs. Schofer, Kelly, Campbell and Mr. C. W. Scammon, Houston Oil Field Material Co., who arranged the entertainment for the dinner, were given a vote of appreciation in recognition of their hard work which contributed in making the meeting a success. The session was then adjourned.

Western Region

The Western Regional Division held their third regular meeting November 5 in Los Angeles. Vance N. Jenkins, Union Oil Company, presided. The meeting was highlighted by announcement of the new officers, who are as follows: Irwin C. Dietze, Los Angeles Department of Water and Power, chairman; C. Kenyon Wells, Long Beach Water Department, vice chairman; C. H. Goldkamp, San Diego Gas and Electric Co., secretary-treasurer. Technical subjects which were covered included the use of Calgon in combating corrosion, a paper presented by Ray L. Sullivan; the delivery of natural gas to Southern California through the "Biggest Inch Pipeline" serving the area; and a color film on galvanizing made by the American Hot Dip Galvanizers Association.

North East Region

The North East Region held their first meeting of the 1947-48 season November 4 in Baltimore, Md. During the one-day session, the following papers were presented: Corrosion Prevention in Long Term Storage of Military Equipment, by Max F. Mueller, Engineering Division, Davison Chemical Corp., Baltimore, which pointed out methods of preserving military equipment in long time storage by use of desiccants; Underground Corrosion of Wrought Ferrous Metals, By I. A. Dennison, Chief, Underground Corrosion Section, Division of Metallurgy, National Bureau of Standards, Washington, D. C., representing tests of 14 years on the influence of metal compositions on corrosion resistance in various underground soil conditions; The Use of Stainless Steel for Corrosion Prevention in Wartime Application, by Thomas L. Moore, Development Engineering Department, Rustless Iron & Steel Division, The American Rolling Mill Co., Baltimore, which constituted case histories of the application of stainless steel to prevent corrosion; and Wartime Experiences With the Use of Magnesium Alloys, by E. S. Bunn, Metallurgical Manager, Revere Copper & Brass Co., Baltimore.

During the business meeting which followed the technical session, the result of the vote on new officers was announced as follows: Regional Chairman (three-year term), E. P. Noppel, Ebasco Services, Inc., New York; Chairman, A. S. Brookes, Public Service Electric and Gas Co., Newark, N. J.; Vice Chairman, R. H. Lynch, Philadelphia; Secretary-Treasurer, L. B. Donovan, Consolidated Edison Co., New York. All new officers will take up their duties January 1, 1948.

South East Region

Alan C. Nelson, Secretary-Treasurer of the South East Region, reported that a nominating committee met November 3 and named James T. MacKenzie, American Cast Iron Pipe Co., Birmingham, Ala., as Regional Director to succeed E. B. Ayers, who was forced to resign because of change of residence to the South Central Region. The committee also nominated Regional officers for the coming year, as follows: Charles B. Gamble, Birmingham Gas Co., Birmingham, Ala., chairman; E. C. Range, The Okonite Co., Atlanta, vice-chairman; E. D. Macaulley, American Cast Iron Pipe, Co., secretary-treasurer. A mail ballot will be conducted, and results announced during a meeting schedule in February 1948, at a time and place to be announced later.

Cleveland Section

The Cleveland (Ohio) Section held its first Fall meeting September 30. R. B. Mears, Carnegie-Illinois Steel Corp., Pittsburgh, and a Director of NACE, was the principal speaker. His subject was Causes of Local Corrosion. Other officers of the Association present were Vice President F. L. LaQue, International Nickel Co., Inc., New York, and Mars G. Fontana, The Ohio State University, Columbus, Director representing the Active Membership and Chairman of the Technical Program Committee for the 1948 NACE Conference and Exhibition. Mr. Fontana told of the work of the Correlating Committee on Corrosion, of which he is chairman.

Tulsa Section

The Tulsa (Oklahoma) Section met October 10. Don B. Good, Texas Pipe Line Co., presided. A discussion of corrosion problems related to oil storage and pipeline tankage was presented by R. E. Clark and J. C. Nicholson, Natasco Company. Mr. Clark discussed the principle causes

Report on 1948 Conference Technical Program

• In a formal report to F. L. Goldsby, General Chairman for the 1948 NACE All-Corrosion show, Mars G. Fontana, Chairman of the Technical Program Committee, revealed that 23 of the 40 papers to be presented during the ten scheduled technical sessions have been definitely accepted, and papers are under consideration for the majority of the positions not presently assigned. The programs have been completed for four symposia—Chemical Industry, Salt Water Corrosion, Electrical Industry and General Industry. Other sessions to be held, and partially completed at the time of the report, are: Cathodic Protection, Communications, Gas, Oil, Protective Coatings for Metals, and Water. With 60 percent of the papers already definite, it is anticipated by Mr. Fontana that all symposia will be completed by December 31, at which time another report will be made. The 1948 NACE Conference and Exhibition will be held April 5 through 8 at the Hotel Jefferson, St. Louis, Mo.

and locations of tank corrosion, while Mr. Nicholson reviewed the economic factors governing methods of protection. Specific cases were cited where protective coatings have been applied to tanks to successfully combat corrosion. Following the discussion, R. L. Bullock read a report of findings of an inspection group that examined a variety of protective coatings and alloys in West Texas field tanks.

Sectional meetings were also held in Shreveport, La., and Corpus Christi, Texas.

PERSONALS

E. S. Merriam, Marietta, Ohio, consultant for the natural gas industry, has joined the faculty of the Marietta College School of Petroleum on a part-time basis. He will teach courses in engineering materials and gas production, distribution and utilization.

Quincy Bent, vice president in charge of operations, Steel Division, Bethlehem Steel Corp., Bethlehem, Pa., retired November 1, after devoting 47 years of his business life to the industry's development. He will continue as vice president in an advisory capacity, and as a director of the corporation until December 31. He is succeeded as vice president by

THE NEWS SECTION was primarily incorporated in Corrosion to provide a record of the current activities of members of the Association, and to convey information of interest and value to members. All members are invited (in fact urged) to send releases, or letters, informing the editors of changes in positions, promotions, achievements, or other news items. All material should be forwarded to the Editor of CORROSION, 905 Southern Standard Bldg., 711 Main Street, Houston 2, Texas.

Stewart J. Cort, who has been a member of the corporation since 1927.

J. R. Corbett, president Cato Oil & Grease Co., Oklahoma City, has been elected president of the National Lubricating Grease Institute. **B. F. Symon,** manager, Lubrication Sales Department, Shell Oil Co., Inc., New York, was named vice president of the Institute.

John Yetter, Link Belt Co., Chicago, Ill., has been named district sales engineer, Ball & Roller Bearing Division of Link Belt, with headquarters in Dallas, Texas. He will specialize on the application of ball and roller bearings to oilfield operating equipment.

Edward F. Everett, Jr., has joined the Marshall-Moorman Development Company, specialists in new applications of fluid catalyst technique. He formerly was a chemical process engineer with the M. W. Kellogg Company.

L. H. Chenoweth has been appointed general manager of the new plastics materials sales division of the B. F. Goodrich Co., Akron, Ohio.

CORRECT ADDRESS

In the article, Non-Destructive Methods for Determining Metal Plate Thickness, which appeared in the October edition of Corrosion, the address of the manufacturer of the Audigage, Branson Insts., Inc., is incorrect in the reproduction of Table I on page 479. The address is Joe's Hill Road, Danbury, Conn., not Danbury, Mass.

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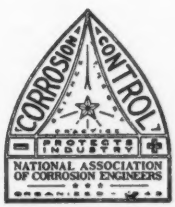

A Message from Your Officers

This Month's Contributor

H. M. TRUEBLOOD, Chairman, Policy and Planning Committee

IT IS THE PARTICULAR business of the Policy and Planning Committee, looking toward the longer future, to develop policies calculated to insure increasingly effective fulfillment by our Association of its obligation to its members and to industry, and to propose plans for putting such policies into effect. It is not going beyond my experience as Chairman of the Committee to say that, up to the present, most of the good leading ideas seem to have occurred already to the capable men who are or who have been at the head of the organization. It would be strange if this were not so. It has not meant, however, that the Policy and Planning Committee has had to live a life of idleness and boredom; quite the contrary has in fact been the case. It would be equally surprising if this in its turn were not so, considering the vigorous state of activity and growth which is so evident in the Association. Indeed one of the strongest impressions a comparative newcomer, like myself, receives from our Association, is that made by this quality of vitality in the Association itself and the enthusiastic interest and willingness to work of its officers.

An equally impressive feature to any newcomer is the evidence very quickly presented to him of the penetrating reach of our subject, corrosion, into practically every work and corner of industrial activity. Although no one with any professional interest in the subject is without some understanding of this, depth and vividness are brought to it by attendance at our conventions in a manner which, I believe, can hardly be equalled otherwise. It is nothing new to say that it is in this universality of our center of interest that our opportunities for the future lie—opportunities some of which have as yet hardly been explored, opportunities to attain the stature and the standing our Association merits among national professional societies.